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Carbon nanotubes in new materials

E G Rakov

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Abstract. Studies of materials consisting of carbon nanotubes or containing them have been analyzed and generalized. Classification of these materials is proposed, their general features and main types are considered, and individual examples are presented. The bibliography includes 372 references.

I. Introduction

Currently, increasing attention is being paid to nanoparticles in modern materials science, as well as in fundamental sciences it is based on, such as physics and chemistry. The reason is wide possibilities of controlling properties of materials without changing their composition. This control is possible due to the manifestation of size effects, which change the electronic, thermal, mechanical, electrical, magnetic, optical and other properties of particles and, correspondingly, affect properties of nanomaterials.†

It is generally accepted to classify compact nanomaterials as nanostructured and nanofilled. The former entirely consist of nanoparticles (nanograins, nanocrystallites), while the latter contain nanoparticles embedded in a matrix and belong to nanocomposites.

New materials with improved properties can be designed by applying nanostructurization and nanoparticle fillers in composites with matrices of different types (polymer, ceramic and metal matrices). This approach extends the range of applications of many conventional materials. In addition, nanoparticles can be used as components of various hybrid materials.

Since the 1990s, researchers paid increasing attention to carbon nanotubes (CNTs) and their close analogue, carbon nanofibres (CNFs). Size effects in CNTs manifest themselves not in the same way as in nanoparticles of other inorganic materials; however, the unique set of properties makes CNTs one of the most promising elements for developing new materials of all basic classes: building, structural and functional, including smart materials[1 – 5] and even metamaterials.‡

It is important that carbon nanofilaments can be used to form and modify materials of various geometric shapes (bulk, film, or fibre-like), as well as porous ones.

Carbon nanotubes are powders resembling soot. Individual nanotubes are generally combined into aggregates, which can often be seen even by naked eye. If CNTs are obtained pyrolytically, aggregates become fragile after removing catalyst particles and can easily be destroyed under load. Thin (single-, double- and triple-walled) CNTs are characterized by the formation of bundles composed of parallel nanotubes. Generally the diameter of CNT bundles does not exceed 100 nm; thus, these aggregates are also considered to be nanoparticles.

However, CNTs generally are not used in the form of aggregates or as mixtures of free individual particles or bundles; they are applied either as structures on substrates

E G Rakov D I Mendeleev University of Chemical Technology of Russia, Miusskaya pl. 9, 125047 Moscow, Russian Federation.
Tel. (7-495) 490 75 24, e-mail: eg_rakov@rctu.ru

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† Below materials are considered as solid substances in the form applicable for civil engineering, fabrication of constructions and working elements of devices. Materials containing nanoparticles or composed of nanoparticles are referred to as nanomaterials.

‡ Materials with artificially formed periodic structure and unusual properties, *e.g.*, negative refractive index.

or as intermediate products in production of various macromaterials. The widespread techniques for consolidating ceramic and metal particles, such as pressing and sintering, as well as overwhelming majority of their modifications, cannot be applied to nanotubes. Therefore, peculiar procedures should be developed to form materials composed of CNTs or containing CNTs (for brevity they will be referred to as CNT materials).

Individual CNTs exhibit an unusual combination of various properties, due to which they can be used as operation elements of many devices and appliances, such as diodes, transistors, switches, logical elements, electrodes, sensors and probes for atomic-force and tunnelling microscopes. However, because of the dependence of electronic properties on the CNT structure, problems with sorting CNTs in morphology and properties [6] (see Refs. 7 and 8 for the latest achievements in this field), expected high cost of sorting and difficulties in selective synthesis of nanotubes with identical structures, one would expect application of CNT arrays and macromaterials (in particular, films [9]) to be more efficient than the use of individual CNTs in the foreseeable future. Using polymer substrates, one can develop flexible devices based on CNT films; this approach extends the range of their applications and gives grounds to speak about flexible electronics based on nanotubes.[10, 11]

In 2005 a competitor of nanotubes arose: graphenes, which are single layers or multilayers (with a limited number of layers) of flat nanoparticles. Properties of single-layer graphene are similar in many respects to those of single-walled CNTs. In contrast to CNTs, many characteristics of which depend on their diameter and chirality, graphenes are easier to sort. However, it is necessary to take into account that graphene properties depend strongly on the type of the substrate they are laid on or the matrix they are inserted into. One might expect graphenes to supplant CNTs in applications calling for individual particles, while CNTs, as previously, will dominate (at least in the nearest future) in the production of materials. The situation may change when commercial graphene production starts; however, even then CNTs will remain among nanomaterials of the highest demand.

CNT materials are easier to introduce into commercial practice than individual nanotubes. The review paper [2] in a hard-to-get book is devoted to specifically these materials. Reviews [12–14] and a section in the report [15] are also partially devoted to the fabrication of CNT materials. However, many new data in this field have been obtained after 2008, so that this huge amount cannot be considered comprehensively in a single review without loss of valuable information.

The purpose of this review was to classify CNT materials and briefly describe their main types, methods of synthesis and ranges of application. The chemical methods and procedures used to produce these materials are not described; however, the main directions of research are outlined. The list of references contains mainly reviews and landmark studies. A majority of references to specific developments can be found in the literature cited.

II. State of the matter and prospects of production of carbon nanotubes

The history of the development of studies in the field of CNTs and CNFs and their production includes several stages. The modern stage, which started approximately at the beginning of the 2000s, is related to the development of CNT industry.[16] This temporal boundary is arbitrary, because, for example, the commercial production and practical application of one of the CNT types began as early as in the 1990s (Hyperion Catalysis Int., the United States), and the fundamentals of one of the methods of CNT production that are currently used in Japan were described by Endo [17] as early as in the 1970s. Numerous pioneer studies by R E Smalley, a Nobel prize winner in chemistry in 1996, contributed a lot to the development of the CNT research. The first publications by Iijima [18, 19] awakened common interest in CNTs.

The number of scientific publications devoted to CNTs steadily increases. Thus, their total number reached 1000 by 2000,[20] amounted to 7000 by 2007 [21] and exceeded 10 000 by 2008.[22]

By 2006 CNTs became the most intensively studied object of physics. Statistical calculations based on the use of a peculiar '*m* index' have shown that, according to this criterion, CNTs (12.85) leave behind nanowires (8.75), quantum dots (7.84), fullerenes (7.78) and giant-magnetoresistance materials (6.82).[22] The conference on CNTs [23] held in 2010 demonstrated that their expansion into various fields of science and technology continues and shows a visible tendency to practical applications.

In recent years, CNTs, as well as more available CNFs and related carbon materials, due to their properties and wide possibilities of application in various branches of industry, have all chances to become one of the leaders (in output) among commercially produced nanomaterials.[24, 25]

According to the report,[26] more than 180 companies produce carbon nanomaterials (including CNTs, CNFs, nanodiamonds, fullerenes and graphenes) and more than 700 companies develop CNT materials for the applications in aviation and space, car, power, defense, medical, textile and other industries, in information technologies and for environmental protection. Single-walled CNTs are expected to replace silicon in electronic chips in 10–15 years.

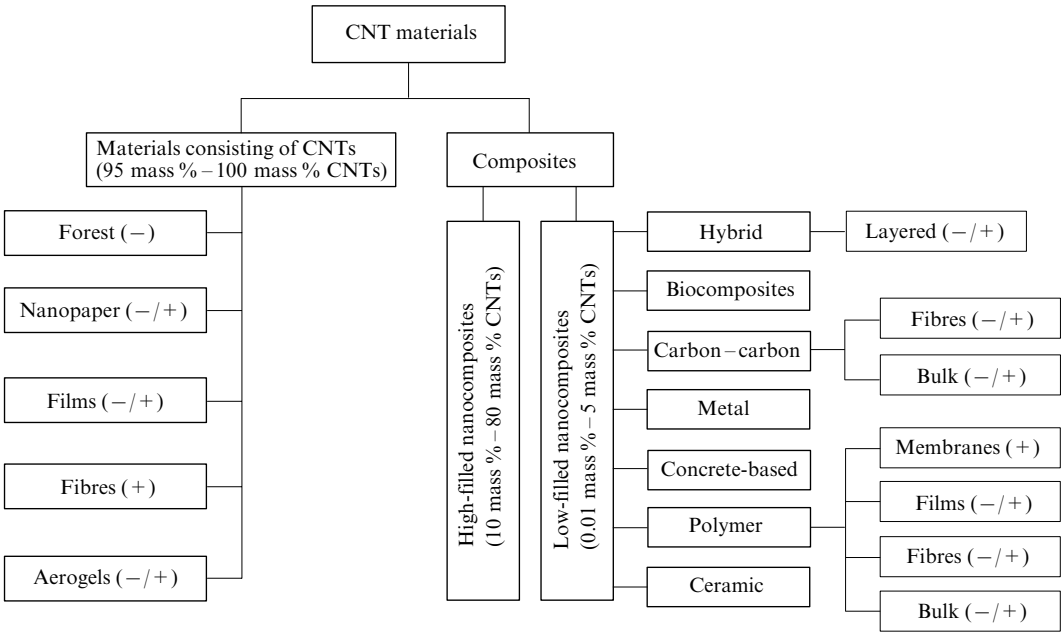
The capacities of some CNT production facilities have reached 500 tonnes per year.[27–29] Facilities with the annual output of up to 2000 tonnes are planned to be developed.

Related CNT materials include nanohorns (tapered-cylinder nanoparticles) and vapour-phase grown nanofibres (according to the data by Wei *et al.*,[13] Showa Denko (Japan) is planning to increase the current production capacity of 100 tonnes per year by 400 tonnes per year), helical and branched forms, *etc.*[28] Below we often arbitrarily use the abbreviation CNT or term 'nanotube' for all filamentary carbon nanomaterials. Only in some cases we indicate the type of CNTs under consideration: single-, double- or multiwalled CNTs or CNFs.

The output of multiwalled CNTs and CNFs is the highest. The total production output, which was 390 tonnes per year in 2008 and 1500 tonnes per year in 2009, increased to 3400 tonnes per year by the end of 2010 and is planned to reach 9400 tonnes per year by 2015.[26] The output of carbon nanomaterials is expected to grow at a higher rate than the production capacities and the cost of these materials is estimated to reduce by 12% a year on average.

The world leaders in the CNT production are Asian countries, whose production exceeds that of European and American countries by a factor of 2–3. Japan occupies the

Scheme 1



first place; in particular, it produces several tonnes of CNTs for lithium-ion storage batteries.

The overwhelming majority of new CNT productions apply processes based on versions of the pyrolytic method, which is considered to be the most efficient and flexible.[11,30–37] One of recent significant achievements of Japan researchers is the development of supergrowth of a 'forest': an array of CNTs on a flat substrate oriented perpendicularly to it.[38–40] The essence of this method is in the simultaneous performance of two processes: the catalytic pyrolysis of hydrocarbons and the etching of minor products (which shield catalyst particles) by small oxidant additives. This allows one to reach very high CNT growth rates, long service life of the catalyst without poisoning and a very high CNT specific output: up to 500 gramme per gramme of the catalyst. In addition, the CNT selectivity reaches 99.5%; the carbon content in them is 99.98%, due to which one does not need to purify CNTs from the catalyst.[41] This technique makes it possible to control the CNT morphology and produce basically single-, double- or multiwalled CNTs.

In 2011 the first pilot manufacturing of CNTs based on the supergrowth technique, with an output up to 100 g h^{-1}, was started in Japan; it is planned to launch the first plant by 2014.[42] Pyrolytic CNTs are obtained in most cases using fluidized catalyst bed or flying bed reactors; currently, a conveyor reactor (of the ribbon-conveyor type) is projected for the CNT production. The expansion of production is expected to reduce the cost of high-quality CNTs by several hundreds of times (to 12 USD for 1 kg) and thus expand their areas of application. Single-walled CNTs are proposed to be used as components of supercapacitor electrodes.

Studies aimed at developing continuous CNT-forest production techniques are carried out in other countries as well.

Processes of the synthesis in fluidized bed reactors are extensively studied. Advances in this field make it possible to reduce the number of process operations, increase the CNT quality and reduce the CNT production cost. Examples are the techniques of CNT growth on vermiculite[43,44] and ceramic microspheres.[45]

A plasma process for producing relatively inexpensive CNFs of low quality has been developed in Belarus.[46]

Against the background of the above-described technologies, the low-output and unprofitable electric-arc and laser-thermal methods of CNT production (they are described, *e.g.*, in the publication[30]) are expected to become nothing more but a turned page in the history of nanotube technique development.§

III. Classification of CNT materials

Carbon nanotubes belong to rare types of materials that can relatively easily be obtained by implementing the following principle of nanotechnology: the bottom-up assembly; *i.e.*, the formation of relatively large particles or products from small particles and their aggregates. These products may consist of macroscopic, most often available for human visual and tactual perception, bulky bodies (three-dimensional aggregates), coatings and films (two-dimensional aggregates) or filaments and fibres (one-dimensional aggregates). Macroscopic objects include also two- or three-dimensional porous bodies (xerogels) and membranes.

CNTs can be used to design structures on substrates, which are promising for electronics and optoelectronics devices, as well as for various sensors.

The general classification of CNT materials was proposed in the publication.[16] It is presented (in supplemented and somewhat modified form) in Scheme 1.

As was noted above, all CNT materials are divided into two classes: materials composed of CNTs and CNT-containing ones. The former materials belong to nanostructured materials and contain generally no more than 5 mass % adhesive additives, while the latter (nanofilled)

§ An example of the way chemical facilities should not be designed is the technically illiterate system of plate-and-hood type for Taunit production from a propane–butane mixture at the Komsomolets plant (Tambov).[47]

materials are composites. The latter materials are arbitrarily separated into high-filled (with comparable concentrations of the matrix material and CNTs) and low-filled (containing no more than 5 mass % CNT) composites. The set of high-filled composites is rather small. Low-filled nanocomposites are considered to be the most widespread and extensively developed CNT materials.

The basic CNT materials include forest, nanopaper, films, fibres and aerogels. Other, less widespread (and, possibly, of less practical importance) CNT materials are 'monoliths', compact sets and three-dimensional framework structures,[48] as well as differently shaped CNT aggregates ('chrysanthemum', 'bird nest', 'bud', 'cedar forest', 'combed yarn'[30]), mesoscale tubes formed as a result of CNT self-assembly,[49] *etc*.

There are several species of CNT forest, which differ in the fabrication technology.

Randomly packed CNTs can be consolidated through their mutual entanglement with the formation of nanopaper¶ ('nanomats', 'nanofelt').

The most widespread second-group materials are nanocomposites based on polymers, ceramics or metals, as well as biocomposites and hybrid materials. This group includes also carbon–carbon nanocomposites. Less attention is paid to the fabrication and study of glass-based CNT nanocomposites.

Hybrid composites form a class related to nanocomposites. Generally, this term is used for composites containing both organic and inorganic materials; CNTs can play the role of inorganic filler.[50] In this context, nanocomposites with a polymer matrix can also be assigned to hybrid composites. Polymer nanocomposites are considered as an individual group because of a large number of their species and the current interest in these materials.

Some CNT-containing biocomposites can also be assigned to hybrid nanocomposites. Some other materials, like biocomposites, can be assigned simultaneously to different classes; hence, the classification proposed here is to a certain extent arbitrary.

At the same time, the properties and ranges of application of each selected group of materials may differ, and these differences are most pronounced for nanostructured materials and nanocomposites.

Nanocomposites, as well as CNT materials, can form bulk objects, coatings or fibres. This is especially true for polymer-based nanocomposites, although one would expect various forms of ceramic and metal composites (for example, ceramic coatings) to arise in future. CNT objects of different shapes have different properties and ranges of application; for this reason, they are also classified in Scheme 1.

The two-dimensional geometry of CNTs allows for two types of their packing: random and with the parallel arrangement of tubes; they are indicated, respectively, by '+' and '−' signs in Scheme 1. Materials with the parallel arrangement of CNTs have the most useful properties, although some cases call for another arrangement, for example, in the form of a network or a product of variable cross-section and different densities of tubes in different cross-sections.

The properties of materials with the parallel CNT orientation differ significantly (and sometimes radically) from the parameters of materials with randomly arranged nanotubes. Thus, the former are anisotropic and are characterized by the highest values of some target characteristics (*e.g.*, thermal conductivity, electrical conductivity, optical and acoustic properties) along the nanotube axes.

The existence of different packings leads to a numerous types of materials, which nevertheless have some general features.

IV. General features of CNT materials

It is not sufficient to define CNTs as a new substance or a new class of substances or even a new class of materials. CNT materials have a number of general features distinguishing them from the variety of other modern materials. The fabrication of CNT materials is a new stage in the evolution of materials science. Currently it is one of the most rapidly developing fields in nanomaterials science. The fabrication of CNT-containing nanocomposites is often referred to as a revolution in materials science.[51] The experts of the Y-12 centre† (Houston, the United States) believe that new-generation composites can be developed based on a combination of metals, cermets and CNT-containing ceramics.

When productive techniques of the CNT synthesis were developed, CNT materials produced using these techniques became objects of extensive study of many researchers (the first publication[52] is dated 1994). In 2002, the first review[12] of such materials (referred to as macroscopic structures in the original) was published. The pioneer in the practical application of CNT materials was apparently the aforementioned Hyperion Catalysis Inc (the United States), the experts of which developed the technology of 'fibrils' (multiwalled CNTs) as early as in the 1980s and then applied them as fillers for some commercial polymers (polybutylene terephthalate, polycarbonate, *etc*.). To date, many foreign companies commercially produce these materials in various forms, and the applied research in the field of CNT materials constantly expands. The total number of publications on them can be estimated as several thousands.

The basic features of CNTs, which manifest themselves in materials, include the above-mentioned ability to form different packing patterns, polyfunctionality, possibilities of varying properties by chemical modification, inapplicability of commonly accepted methods for the particle consolidation, the tendency to aggregate and the structuring effect of CNTs on the adjacent matrix layers, which manifests itself in a number of nanocomposites.

Nanoparticles of different composition (metals, oxides, carbides, *etc*.) are also used to form composites and compact sets. However, except for CNTs and their analogues, none other type of nanoparticles can be assigned to polyfunctional, none other fits so well for technical application in the composition of various materials and suits for such a variety of materials. However, in a rather short time, the

¶ In the literature this material is most often referred to as 'buckypaper', because the term 'nanopapers' is also used for materials composed of cellulose or artificial polymers if the fibres forming these materials are less than 100 nm in diameter.

† This centre is known for its studies in the field of nuclear weapons; currently, the main research directions are nanotechnologies and nanomaterials.

class of CNT materials will be supplemented with graphenes.

The polyfunctionality of CNTs is due to the peculiar set of their electronic, mechanical, transport (thermal and electrical conductivities), thermal and chemical properties.[30] Depending on their structure, nanotubes may have electric conductivity of metal or semiconductor type. The conductivity of defect-free CNTs may have a ballistic character and not obey Ohm's law. The semiconductor properties depend on the nanotube diameter. Young's modulus and the thermal conductivity of single-walled CNTs exceed the corresponding parameters of most other materials. These and other properties allow one to design CNT materials for different purposes.

One of the methods of targeted changes in the properties of CNT materials is their functionalization *via* the covalent attachment of different functional groups to the lateral surface of tubes. Functionalization of CNTs may enhance their binding to the matrix and change mechanical and electrical properties of the composite. Chemical modification of CNTs (see, *e.g.*, Ref. 53) changes their properties and expands the range of application of CNT materials. In particular, magnetic nanopaper and materials with peculiar sorption, antiseptic and other properties have been developed.

If functional groups can form bonds with each other (*e.g.*, carboxyl groups) or are bifunctional (*e.g.*, diamines), neighbouring CNTs can be interlinked due to this bonding, thus reinforcing the composite.

The fabrication of materials with uniformly distributed CNTs is hindered by the tendency of individual nanotubes to aggregate due to van der Waals interactions. These interactions are fairly strong for CNTs. Aggregates of parallel tubes exhibit a structure, which is often referred to as a two-dimensional crystal lattice. Long single-walled CNTs of high purity exhibit the strongest linking. If the number of walls exceeds 3–4, the interaction between CNTs is much weaker. Tubes with conically arranged graphene layers and nanofibres can hardly be linked due to the van der Waals forces.

The character and strength of binding of individual CNTs with the matrix material, as well as the structuring effect of tubes on the matrix, are of great importance.

As was noted above, conventional methods for consolidating nanoparticles, applied to metals or metal oxides (pressing and sintering), are unfit for CNTs. Therefore, to form, *e.g.*, compact sets, spark-plasma sintering is most often used.

V. Materials consisting of carbon nanotubes

The group of materials composed basically of CNTs and containing additives in small amounts (or having no additives at all) include three-dimensional ('monolithic' or porous bodies and bulk aerogels), two-dimensional (coatings, films, nanopaper and flat aerogels) and one-dimensional (micro- and macrofibres) aggregates. Forest and thin membranes consisting of open-tip CNTs occupy intermediate position with respect to dimensionality.

There are only few publications on CNT-based 'monolithic' macromaterials and bulk aerogels; the reason is the difficulties with sintering CNTs or their bonding using other conventional techniques. Monoliths can be obtained by plasma-spark sintering at high temperatures (1000–2000 °C) and pressure (40–80 MPa).

Aerogel is formed from CNT dispersions by two methods: sublimation drying and drying in supercritical solvents. Introduction of polyvinyl alcohol (1 mass %) into initial aqueous CNT dispersion gives rise to products with a relatively high strength and electrical conductivity. The aerogel density is 10–30 g dm^{-3} without polymer additives and 40–60 g dm^{-3} with additives (Fig. 1).[54] Later an aerogel with a density of 4 g dm^{-3} was developed.[55] Sublimation drying was used to obtain aerogels containing silk fibroin additives.[56]

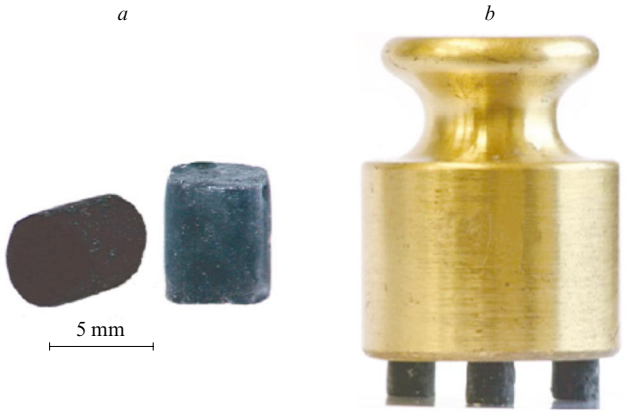


Figure 1. Products made of aerogel.[54]
(*a*) General view and (*b*) three aerogel cylinders with a total mass of 13 mg withstand a 100-g load.

It was noted that some materials composed of entangled long CNTs exhibit viscoelastic behaviour,[57] which manifests itself in an unprecedently wide temperature range: from −196 to 1000 °C. The store and loss moduli of these materials and their stability to load cycling and destruction do not change in the temperature range from −140 to 600 °C.

Coatings, films and nanopaper are related materials as regards their structure and fabrication techniques. With regard to production technology, there are two groups of coatings: the ones obtained directly during CNT synthesis and those formed from CNT dispersions. The first-group materials are obtained at elevated temperatures, using preliminary deposition of catalysts on substrates. If catalyst particles are located along the lines perpendicular to the direction of the gas flow (which has a certain velocity), the CNTs synthesized on the substrate can be oriented along the gas flow direction. This procedure allows one to obtain superlong tubes (Fig. 2).[58–65]

Techniques for fabricating films of closely arranged parallel CNTs by this method have been developed.[66, 67] In particular, a cyclic process allows one to obtain single-walled CNTs on a substrate with a packing density of 20–40 μm^{-2} (Ref. 68; a similar process was also described in Ref. 69).

To prepare CNT elements for devices, a catalyst is deposited in the form of certain geometric figures, using modifications of lithography, nanolithography, or screen printing methods. Techniques for transfer coatings with one substrate to another have been developed (Fig. 3; see Refs

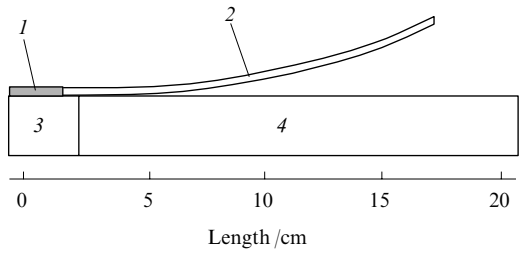


Figure 2. Superlong CNTs obtained by directed gas flow pyrolysis.[64]
(*1*) Catalyst layer, (*2*) CNT, (*3*) catalyst-containing substrate and (*4*) free substrate.

70 and 71–84). Structures consisting of superimposed layers with parallel orientation of CNTs in each layer and different orientations of tubes in different layers have been described.

A version of pyrolysis with a flying catalyst (aerosol synthesis) is not widespread, although it allows one to grow films by filtering reaction gases and transport the films grown to different substrates.[85]

The transfer method was used to obtain films with closely arranged parallel CNTs.[69]

Nanopaper is most often obtained from CNT dispersions rather than from the gas phase. Sheets, sheetlets and disks from 10 to 100 μm thick are formed in several ways. The basic techniques are filtration of dispersions through fine-pore filters and aerography (air sputtering) of dispersions. Much less popular techniques are slow pulling of substrates from dispersions with simultaneous drying; deposition of dispersions on a rapidly rotating disk with subsequent drying; and colloidal methods, for example, coagulation of aqueous dispersions with ethanol added, when a film floats up to the surface and can be removed. The density and porosity of nanopaper can be controlled in certain limits.[86]

Either single-walled or multiwalled CNTs are used to produce nanopaper. In some cases nanopaper made of double-walled CNTs is preferred,[87,88] which has a much larger specific volume and a larger specific surface area of micropores, as compared to the paper made of single-walled CNTs.[89]

Thin (0.1 mm) disks of small diameter (40, 125 and 175 mm) made of nanopaper with a density of 0.5 g cm^{-3} have been produced by NanoLab since 2002. A technology of fabricating sheets with a relatively large area and fairly wide nanopaper ribbons have been developed, as well as machines for continuous production of paper rolls. Sheets with an area of ~ 3 m^2 have been produced by Nanocomp Technologies (the United States) since 2008. The tensile strength of this nanopaper without adhesive depends on the orientation of individual CNTs and ranges from 500 MPa to 1.2 GPa. The density of this nanopaper is twice lower than that of aluminium. The aforementioned company is planning to organize nanopaper production with an output of 6 tonnes per year by 2013.

The nanopaper formed from dispersions may consist of CNTs with parallel orientation. This packing is obtained by different methods, using a magnetic or electric field, capillary forces, or liquid flow. The method for growing thin films with closely arranged parallel CNTs in a magnetic field was described, for example, in Ref. 90.

A micrograph of a multiwalled material, referred to as a nanobook (buckybook), is shown in Fig. 4.

Obviously, the strength of nanopaper made of CNTs without adhesive or without chemical functionalization of nanotubes is low; it is determined by the length of particles and their packing density. To date, different techniques for increasing the nanopaper strength have been developed.[92]

Nanopaper can be applied in filters, which can remove even viruses from water[93] and efficiently perform gas dedusting. It fits also for contact membrane distillation of liquids.[94] Nanopaper coatings are also applied to absorb and scatter electromagnetic radiation and to protect planes from lightnings. Details of electric heaters, high-sensitivity elements of sensors, effective actuators (including artificial muscles[95]), electrodes of electrochemical devices, components of organic LEDs, catalyst supports, fillers of composites with polymer or carbon matrices and many other products are made of nanopaper. Nanopaper is also used as a medium for growing biological tissues and components of bandaging materials for medicine.

A simple technique for producing nanopaper in the form of cylinders with circumferentially arranged CNTs has been developed.[96]

Superthin transparent conducting films and coatings, which were analyzed in many studies,[97–113] have peculiar

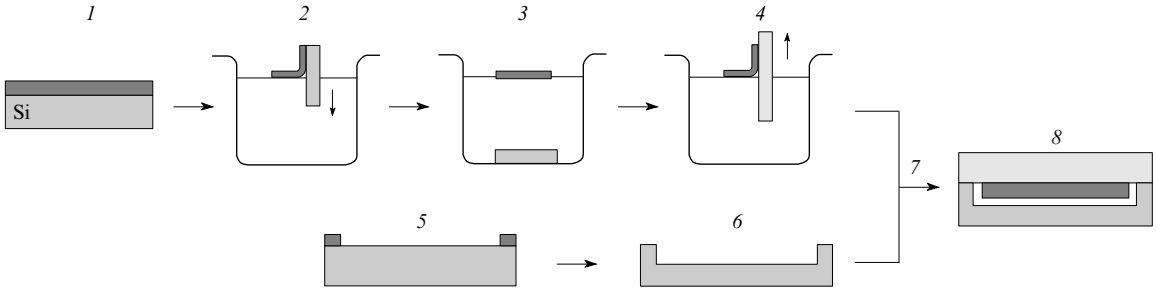


Figure 3. Stages of CNT film transport to other substrates.[70]
(*1*) Growth of a single-walled CNT film on a silicon substrate, (*2*) separation of the film from substrate, (*3*) floating film, (*4*) deposition of the film on a Pyrex glass substrate, (*5*) photolithography of a new silicon substrate, (*6*) etching of the new silicon substrate, (*7*) connection of two elements and (*8*) anode connection.

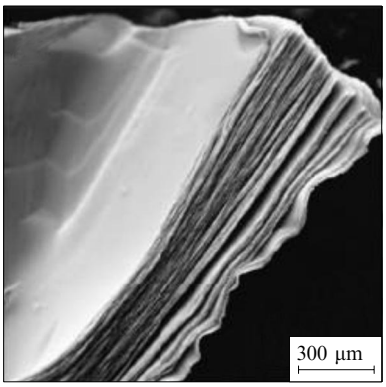


Figure 4. Buckybook made of single-walled CNTs.[91]

applications in electronics and photonics. Methods for forming and modifying them and the ranges of their application were described in reviews.[71, 104, 114] The technical characteristics (transparency and conductivity) of these films make them competitive with solid solutions of indium (90%) and tin oxides.[115] Since 1999 to 2009 the cost of indium significantly increased; therefore, this competition is economically important.[116] CNT films surpass oxide films obtained by different methods, including those formed from dispersions using the inductively coupled plasma technique.

A technique of oriented packing CNTs on flexible substrates in order to design thin-film transistors was described.[117] The Eikos company (the United States) developed (and has been producing since 2005) the 'Invisicon™ ink' compositin for depositing thin CNT films on substrates.[118] Technologies of continuous production of these films are under way.[119]

The electrical conductivity of thin CNT films can be increased through their functionalization.[120] Iodination (which; however, was performed on only CNT fibres) made it possible to reduce the electrical resistance of CNT films to $\sim 10^{-7}\ \Omega$ m at a current density of $10^4 - 10^5$ A cm^{-2}; this achievement opens way for replacing copper wires with carbon ones.[121]

The ranges of application of thin CNT coatings and films include electronics, sensorics, power engineering (solar batteries,[122] electrochemical devices[123]). Films and nanopaper are promising materials for electroluminescent devices,[124] anticorrosion protection components, *etc.*[69] The weight of a CNT solar sail with an area of 1 km^2 for space probes can be as low as 30 kg. Production of smart materials, including electroactive ones, is expected to be an important range of application of CNT films and nanopaper.[125]

It was proposed to use CNT fibres to form a kilometres-long space rope and a lift to deliver loads to a near-Earth orbit. However, many problems must be solved to implement this project .

Methods for producing CNT fibres were reviewed.[126] The following groups of fibres can be selected with regard to the fabrication technology:[14, 127, 128]

— fibres obtained from aerogel formed during hydrocarbon pyrolysis;

— fibres 'condensed' from dispersions and colloidal solutions by coagulation and pulling;

— fibres formed by spinning from ordered-tube arrays (forest).

Aerogel ('elastic smoke') is obtained continuously during CNT synthesis with a volatile catalyst under certain conditions. It differs from aerogels formed from dispersions (see above) by the character of CNT packing and properties. Pyrolysis is performed using a catalyst precursor solution (for example, ferrocene in aromatic hydrocarbons), which is supplied in the dispersed state to the hot zone of the reactor.[129] Fibre is continuously pulled and twisted from the aerogel formed in the reactor. Even in the beginning of 2004 it was reported that macroscopic fibres up to 100 m long can be obtained using this method. Methods for compacting and strengthening the primary fibre are developed.[130–132] Strong fibre has been obtained using the continuous technique (Fig. 5).[133] Fibres were also obtained from entangled CNTs grown on a substrate.[134]

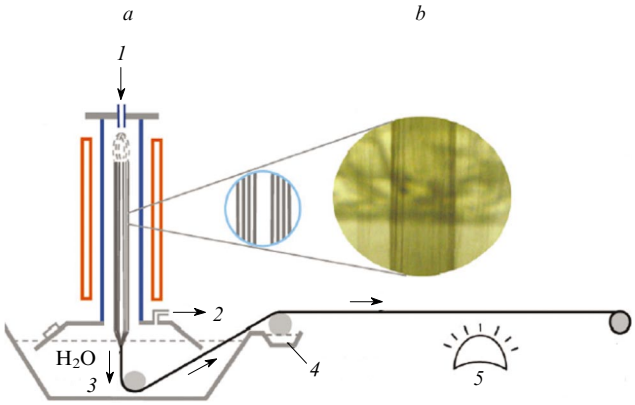


Figure 5. Schematic diagram of the formation and hardening of CNT macrofibre.[133]
(*a*) Reactor for pyrolysis and fibre drawing from aerosol formed and (*b*) schematic fibre texture; (*1*) reactants, (*2*) fitting for removing reaction gases, (*3*) water bath, (*4*) vessel with acetone, and (*5*) IR lamp.

The following record values of tensile strength were reported: 3.3 GPa for fibres obtained from a CNT forest and 8.8 GPa for fibres grown directly from the gas phase; however, reproducible values for long fibres did not exceed 1.23 GPa.[135] The characteristics were somewhat improved by infiltrating polyvinyl alcohol or polyamic acid into the initial fibre.[135] Stronger fibres were obtained using polyethylenimine-catechol, an analogue of natural adhesive polymers, which reinforce mussel shells.[136]

Characteristics of CNT fibres can be improved by thermal treatment.[137]

CNT fibres are obtained from dispersions using electrophoresis and dielectrophoresis, as well as extrusion of dispersions into a concurrent liquid flow, which forms tangent stress and simultaneously extracts solvent from the dispersion.[138, 139] Pulling from dispersions is also applied (see, *e.g.*, Ref. 140).

Promising colloidal systems are considered to be 'solutions' of single-walled CNTs in superacids (100% H_2SO_4 with SO_3 dissolved in it,[141] HSO_3Cl) and some other substances.[142]

Nanocomp Technologies, Inc. (the United States) supplies strong fibres up to 10 km long, which are formed from long CNTs. Twisted filaments have a strength of 3 GPa;

their crack resistance exceeds that of Kevlar (Russian analogue Rusar) and Twaron fibres. This company has demonstrated antennas twisted from native fibres.

Conducting fibres based on modified CNTs are expected to replace metals in the electric mains of spacecrafts and planes (the total length of cables in each Boeing-787 plane amounts to 90 km).[121]

Macroscopic CNT fibres have been obtained from the lyotropic liquid-crystal phase by coagulation in liquid.[143]

CNT forest was initially quite reasonably assigned to films and coatings. However, after discovery of the supergrowth principle,[38] which makes it possible to obtain arrays of long parallel CNTs, the forest is passing (or has already passed) to the category of three-dimensional objects. The supergrowth is implemented by choosing appropriate compositions of the initial gas mixture and substrate and the conditions providing simultaneous occurrence of two processes: CNT formation and etching the carbon shell on catalyst particles.[144] Under these conditions, high-purity tubes 8 and even 15 mm long are formed at a high rate (Fig. 6), their diameter can be controlled, and the catalyst can be used with a high efficiency.[40]

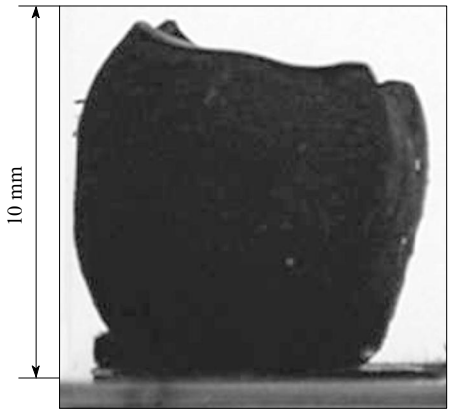


Figure 6. CNT forest.[145]

Along with the growth on a catalyst-covered substrate, forest can be obtained by pyrolysis using a flying catalyst or by a matrix method, applying porous Al_2O_3 membranes.

There are many studies devoted to the formation of micro- and nanorods and nanotubes from different inorganic materials (*e.g.*, Si, Ge), oriented perpendicularly to the substrate. Regularities of the growth of these structures according to the vapour–liquid–solid mechanism were studied and the synthesis of forest from polymers (in particular, from polymerized 2-hydroxyethyl methacrylate[146]) by the matrix method was described; however, concerning the set of functional possibilities and the potential range of application, none other material can compete with CNT forest. Methods have been elaborated for controlling the CNT density in a forest in the range from 10^5 to 10^{13} cm^{-2} and processes of continuous growth of forest on relatively large areas are being developed.

Different techniques for modifying CNTs in forest and transporting the latter from one substrate to another have been described.[147] The forest structures grown on a locally deposited catalyst, before and after modification using the capillary effect, are shown in Fig. 7.[148]

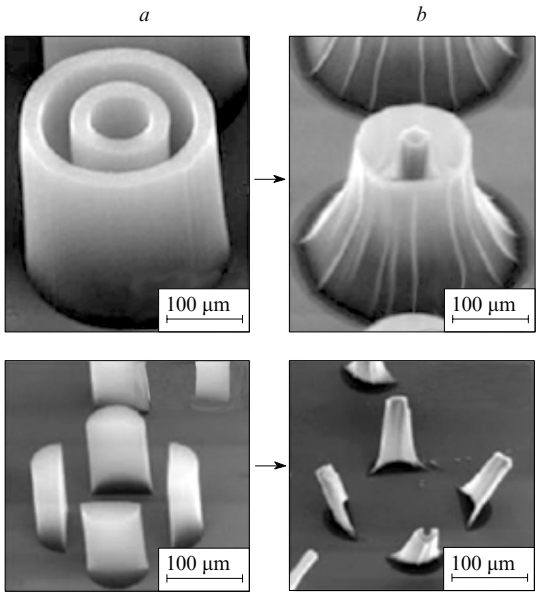


Figure 7. Forest structures (*a*) before and (*b*) after capillary compression.[148]

The potential areas of application of CNT forest are fairly wide and diverse: supercapacitor electrodes and field emitters, current collectors in solar batteries, base of photonic crystals,[149] components of composites, raw material for macrofibres, dense ribbons and membranes and coatings for camouflaging complex-shape objects.[150] Composite fibres, containing metal nanoparticles and having a rather high electrical conductivity, have been obtained.[151] Mechanical packing of forest parallel to the substrate surface makes it possible to fabricate dense ribbons.[152, 153] A forest of open-end CNTs after compacting is a base for membranes with a very high permeability, which are used to separate gas mixtures.[154] As applied to gas separation, forest membranes turned out to be more efficient than nuclear polypropylene membranes with a pore size of 10 nm.

In the first publications pulling macroscopic films and fibres from a CNT forest was compared with the ancient technology of forming silk filaments from silkworm cocoons.[155, 156] However, the mechanisms of these two processes are different; the mechanism of CNT material production is based on the van der Waals interaction between tubes. One of the ways of forming macrofibres from a forest is shown in Fig. 8.[157, 158]

It was believed that not any CNT forest is fit for pulling fibres,[159–161] nevertheless, fibres were obtained even from a powder-like CNT material.[162]

Forest is also used to pull ribbons with nearly coaxial arrangement of CNTs (Fig. 9).[163] The fabrication technology and properties of CNT films (ribbons) were described in the publications.[164, 165] These materials are applied to form artificial muscles, which can operate at temperatures from 80 to 1900 K and provide very high (giant in terms of the authors) elongations and elongation rates: to 220% and 37 000 % s^{-1}.

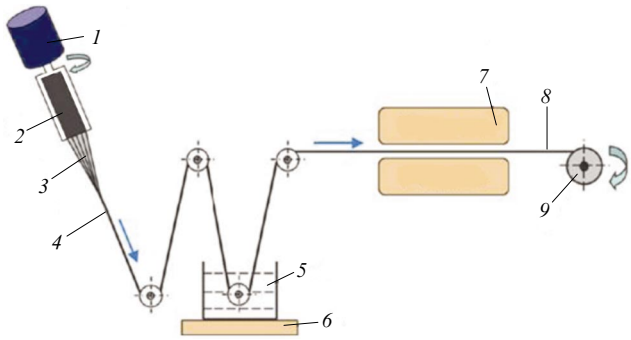


Figure 8. Schematic diagram of the formation and hardening of macrofibre from CNT forest.[157, 158]
(*1*) Rotating spindle, (*2*) substrate with forest, (*3*) drawn filaments, (*4*) twisted macrofibre, (*5*) bath with liquid, (*6*) heater, (*7*) furnace, (*8*) hardened macrofibre and (*9*) coil.

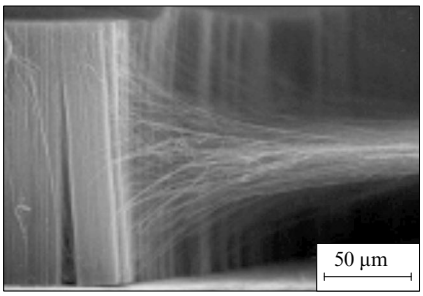


Figure 9. Micrograph of a ribbon drawn from a forest.[163]

The technique of transfering (printing) a forest, grown on catalysts of certain geometry, to another substrate was used to obtain thin films of specified shape.[166] Flat dense ribbons (coatings) with parallel arrangement of CNTs on substrate were obtained from a forest. The main stages of this process are shown in Fig. 10.[167]

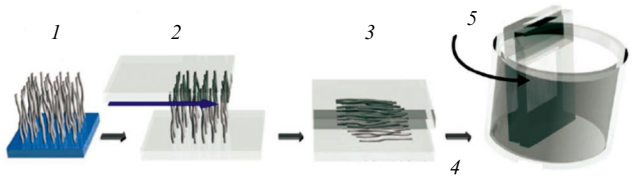


Figure 10. Schematic of the formation of coatings from closely arranged parallel CNTs.[167]
(*1*) Initial forest, (*2*) superposition of a plate, (*3*) 'smoothed forest', (*4*) liquid-aid compacting and (*5*) electrode.

The strength of CNT macromaterials can be increased using small additives of polymers (for example, polyvinyl alcohol, polyvinylidene fluoride, epoxy resin, *etc.*), as well as grafting of oligomers. Nanotubes in coatings and films can be linked *via* a thin shell of polymers, which do not form covalent bonds with nanotubes.

VI. Polymer nanocomposites with carbon nanotubes

The term 'nanocomposites' arose at the end of the 1980s. The interest in this new field of materials science has sharply increased since the mid-1990s. Nanocomposites can be based on polymer, ceramic, or metal matrices; they are applied in the form of coatings, fibres and bulk products.

Polymer nanocomposites are most widespread. The market of various polymer-based nanocomposites increases annually by 24% on average; it had been predicted to reach 500–800 million USD by 2011.[168] The production of CNT-based nanocomposites also rises.

Nanocomposites based on commercial polymers and CNTs radically differ from composites with conventional fillers and composites filled with nanoparticles of other types.[169] These differences are due to the sizes, shape, properties and the well-developed surface of nanotubes. Nanotubes have low density; their specific features are large specific surface area and surface-to-volume ratio, as well as a very large aspect ratio. As was noted above, many CNT types are characterized by unprecedently large values of mechanical characteristics, electrical conductivity and thermal conductivity; therefore, some researchers refer to CNT composites as 'supermaterials'.[170]

Good prospects of CNTs as fillers became obvious after their properties were perceived. Since 1991 to 2000 there were only ~100 publications devoted to composites based on CNT-containing polymers. Then their number started growing sharply: 80 in 2001, 160 in 2002 and > 300 in 2003.[2] By 2010 no less than 50 CNT composites with different polymer matrices had been described. At least ten foreign companies, including such big ones as Bayer (Germany), produce composites with nanotubes. Commercial reviews on the state of nanocomposite market were published in 2008.[171, 172] Numerous reviews on CNT composites arose (see, *e.g.*, Refs 129, 168–184), including reviews of patents,[175] and reviews of polymers with parallel CNTs[176] and structures of different 'dimensionality'.[128]

Nanocomposites based on CNT-containing polymers can be classified according to their application into building, construction and functional ones. The number of building nanocomposites is relatively small; examples are polymer concrete with CNTs and CNT-containing epoxy resin for connecting construction elements. For these composites, as for the second-group ones (in particular, high-strength composite fibres), the most important parameters are mechanical characteristics. Functional composites are designed based on such CNT properties as high electrical conductivity, thermal conductivity and heat resistance, as well as the ability to emit electrons and absorb impact energy and electromagnetic radiation.

The role of CNTs in polymer-based composites is diverse:[3] nanotubes stiffen composites due to their high modulus of tensile strength (~1 TPa); having high elastic strain, they significantly increase the ultimate tensile strength of polymers. The CNT ability to increase hardness and shock strength exceeds even that of carbon fibres. Introduction of CNTs may increase hardness, although their ambiguous effect on this characteristic was noted in some studies. A significant increase in the store modulus has been described.

In the case of chaotic CNT arrangement, the modulus of elasticity of composite increases only slightly in comparison

with that of the initial polymer, whereas functionalization and oriented packing of CNTs lead to better results.

Introduction of CNTs into epoxy resin increases the fatigue strength of composites, which is especially important for aviation materials. The possibilities of using CNTs in aircraft composites were considered,[185,186] and their applications in space industry were reviewed.[187] Replacement of conventional adhesives used in aircraft and space industries with CNT composites looks very promising. In April, 2008 Unidum Inc. (the United States) announced the first flight of Giles G-200 plane with CNT-reinforced airframe details.

Along with CNTs, CNFs are also used to produce nanocomposites. Below some ranges of application of these materials are listed.[188]

Military applications	Civil applications
Nanocomposites based on synthetic rubber	
Tank tracks, aircraft tyres, parts of ships	Car and aircraft tyres, parts of ships, sporting equipment
Nanocomposites based on thermoplastic or thermoset polymers	
Parts of planes, satellites, ships and optical devices	Car bodies, sporting equipment, details of optical devices
Nanocomposites based on epoxy resin	
Airframes	Sporting equipment, details of vehicles

CNT composites can be used as damping materials in motor industry, aviation, navy and aerospace industry.[189–191] Nanotubes have peculiar tribological characteristics.[192,193]

CNT-reinforced polymers and hybrid composites are promising ballistic materials, for example, for bullet-proof vests. Three ways were proposed to form protective means: introduction of CNTs into a polymer adhesive, use of CNT macrofibres in composite and reinforcement of conventionally used polymer fibres with nanotubes. Nanocomp Technologies (the United States) has launched production of bullet-proof vests made of CNT-containing fabrics.

Nanotubes are an exceptional material for making polymers electrically conductive. The minimum concentration of conducting filler in an insulating matrix at which the composite conductivity starts increasing (the percolation threshold) is determined by the particle shape; in the case of CNTs it can be reduced to 0.0025 mass %.[194] For comparison, the percolation thresholds of soot and carbon fibres are, respectively, 15 mass % – 20 mass % and 9 mass % – 18 mass %.

Conducting CNT-containing glues are promising for aircraft construction. Making polymers electrically conductive allows one to remove static electricity charges, as well as absorb and scatter electromagnetic radiation.[195] Even in 2007 about 60% cars produced in the United States were equipped with fuel pipes made of CNT composites, which reduced the risk of explosions caused by charge accumulation.[170] Introduction of small amounts (0.15 vol.%) of CNT additives into polymers makes it possible to monitor the crack formation in a composite by analyzing its conductivity.[196]

Below we present some fields of application of conducting composites with CNFs.[188]

Military applications	Civil applications
Removal of electrostatic charges	
Satellites, fuel hoses, pipelines and seals	Fuel hoses, pipelines and seals for cars, protection of electronic equipment
Electrostatic painting	
Planes, ships, ground-based vehicles	Parts of cars and planes
Protection from electromagnetic radiation	
Avionics, safety systems and reduction of accident rate	High-speed computers, communication facilities
Lightning protection	
Planes (especially the ones with composite airframe), ships, radar shells, artillery bunkers	Planes and ground-based buildings
Flexible contacts	
Parts of solar batteries, electronic devices	Electronic devices

An important and promising property of CNT composites is their elevated thermal conductivity. However, in some cases high thermal conductivity of CNTs cannot be implemented in composites. It was proposed to introduce low-defect (annealed at a high temperature) or shortened CNTs into composites to obtain high thermal conduction. When introducing 3 mass % CNTs, the thermal conductivity of polycrystalline polyurethane can be increased by a factor of more than 3: from 0.15 to 0.47 W (m K)$^{-1}$ (Ref. 197). Below we list the ranges of application of polymer-based composites with a low coefficient of thermal expansion and high thermal conductivity.[188]

Military applications	Civil applications
Optical tools	
Cast mirrors, lasers	Cast optics
Parts	
Parts of satellite-orbit stabilization systems and gyroscopes of planes, ships and ground-based machines	Metal-compatible parts of cars, ships and planes
Electronic devices	
Control stations, board equipment, power electronics	Household electronics, computers, cooling systems

CNT composites are highly stable to ignition, and many of them exhibit elevated chemical, photochemical and radiation resistance. Combustibility was decreased by introducing CNTs into polystyrene,[198–200] polyethylene,[201] polypropylene[202] and other polymers.[203,204] Composites can be used as a base for electrodes of lithium-ion batteries and supercapacitors, membranes of fuel cells,[205] various sensors,[125,206–208] electric and optical actuators,[209–211] and optical limiters for lasers.[212,213] Introduction of CNFs into a material may reduce its coefficient of thermal expansion.[214] Studies of CNT-containing polymer composites for ultrafast photonics were generalized in review.[215]

The effect of fillers is local and related in many cases to peculiar structurization of polymers, change in their struc-

ture, texture and fraction of crystalline phase. A fairly thick coating is formed around CNTs, whose external diameter significantly exceeds that of nanotubes; this coating changes the mechanical properties of the initial polymers and affects the composite characteristics. CNT-induced crystallization of polymers may lead to the formation of globular or lamellar crystals, as well as periodic structures of the 'shish kebab' type. We believe the study of the CNT polymer interface properties and the interaction between nanotubes and polymer matrix to be one of the most important areas of the nanocomposites science.

CNT-containing polymer nanocomposites are obtained in several ways, including solution and melt methods. CNTs can most easily be introduced into thermoplastic melts. This method makes it possible to use extrusion, mixing in closed vessels, cast moulding, or blow moulding and does not call for solvents.

CNTs are introduced into solutions using mechanical or magnetic stirring, as well as intense ultrasonic treatment. As in the melt method, this technique has some limitations, related to the sharp increase in the viscosity of the system. The solution method is used to obtain, for example, composites based on epoxy resins. Latex technique can be considered as a modification of the solution method.

The frequently used methods are preliminary functionalization of CNTs, grafting monomers and oligomers to their surface with subsequent polymerization of these groups, *etc*. Seven 'grafting-to' methods and ten 'grafting from' methods were described in review.[181] In the first-group methods previously formed polymer chains with a certain molecular mass react with functionalized CNTs. Drawbacks of these procedures are the low surface density of associated chains and limitations in the choice of polymers, whose molecules must have terminal reactive fragments. The second-group methods imply polymerization under the action of initiators attached to CNTs. In this case, there are no steric limitations on the formation of polymers with a large molecular mass and high surface density.

Examples of application of radical and emulsion polymerization; electropolymerization; and plasma, radiative and autoclave polymerization can be found in the literature.

Techniques for preparing composites with a high CNT content are as follows: infiltration of nanopaper[216,217] or CNT forest,[218,219] and freezing and freeze drying of dispersion.[220] Thin composite films can be obtained by ultrasonic deposition of dispersions.[221] Two-layer forest films on polyurethane have been developed[222] (Fig. 11).

Many polymers can envelop CNTs and transform them into dispersions (solubilize). This behaviour was observed for polyphenylacetylene, poly(*p*-phenylene vinylene) and its copolymers, polyvinyl pyrrolidone and polystyrene sulfonate, polyethylene glycol with oligothiophene, amylose, cellulose, carboxymethylcellulose and starch.

Flexible conducting CNT films with Naphion are superhydrophobic.[223] Strong conducting paper has been developed based on cellulose fibres and CNTs.[224] The transparency of thin composite films was improved by shortening single-walled CNTs.[225] Transparent films based on polyvinylidene fluoride can be used as membranes of loudspeakers and microphones.[226] Layered composites in the form of thin coatings and films were prepared using layer-by-layer deposition of functionalized CNTs and polyelectrolytes.

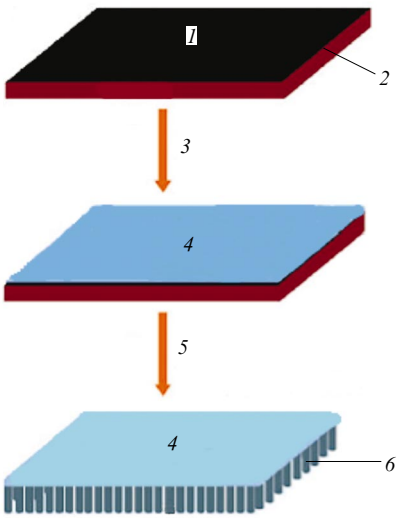


Figure 11. Schematic of the formation of a composite polyurethane film with CNT forest.[222]
(*1*) Forest, (*2*) silicon, (*3*) filling with polyurethane, (*4*) polyurethane layer, (*5* removal of silicon and (*6*) forest on polyurethane.

Among polymer-based composites, note membranes made of open CNTs.[227,228] One of the methods for fabricating these membranes implies CNT packing in magnetic field.[229]

Composite fibres based on CNT-containing polymers are expected to find wide application.[128] These fibres are obtained by conventional methods of moulding from solutions and melts, applying spinnerets or electroforming, from polymer-coated CNTs,[230] or using impregnation of CNT macrofibres with a polymer.[231] Electroforming of composite fibres based on many CNT-containing polymers is used to obtain porous membranes (see, *e.g.*, Ref. 232).

VII. Inorganic composites with carbon nanotubes

Ceramic CNT-containing composites have been developed based on Al_2O_3, $Al_2O_3-ZrO_2$, Al_2O_3-SiC, ZnO, SiO_2, SnO_2, TiO_2, ZrO_2, $ZrO_2-Y_2O_3$, $MgAl_2O_4$, $FeAl_2O_4$, $BaTiO_3$, V_2O_5, $CoFe_2O_4$, SiC, $SiC-ZrB_2$, B_4C, BN, Si_3N_4, TiN, MgB_2, MoS_2 and other compounds; many of them were described in reviews.[233–236] Much attention is paid to hydroxyapatite-based composites, which are applied in bone prostheses.[237]

Co_3O_4–CNT aerogel has been synthesized.[238] Many composites are assigned to functional materials (for example, CNT-containing piezoelectric ceramics). The properties of polyfunctional ceramic composites were discussed.[239]

Ceramics-based composites can be obtained using conventional methods: synthesis from initial powders, preparation of mixtures, moulding and sintering. CNT-containing mixtures are prepared in different ways, including colloidal methods and electrophoresis. Hot pressing or spark-plasma sintering are used in the final stage. Spark-plasma sintering in an inert medium turned out to be the most appropriate technique. It is based on several effects: generation of a spark plasma, spark shock pressure, Joule heating and diffusion induced by electric field. This technique provides densities of material close to the theoretical limit.

There are peculiar methods for forming composites using previously decorated CNTs. They make it possible to obtain ceramic nanotubes and nanorods and synthesize CNTs on oxides containing metal catalyst nanoparticles or directly on oxides (see, *e.g.*, Ref. 240). Decoration from solutions can be performed under supercritical conditions. Composites are also obtained using precursors, in particular, materials that decompose to oxides.[241]

Methods for fabricating sandwich, layered and gradient CNT-containing ceramics are more complicated. Ceramic composites can also be obtained in the form of coatings (see, in particular, study,[242] where jet plasma spraying was described).

As in the case of polymer composites, the most difficult problems to be solved are uniform distribution of CNTs over matrix and optimal strength of their linking with the matrix.

Even small CNT additives increase the crack resistance, electrical conductivity and thermal conductivity of ceramics and make them able to protect from electromagnetic radiation. For example, introduction of 1 mass % CNT increases the toughness of $BaTiO_3$ by a factor of 2.4, and introduction of 10 vol.% CNTs increases the electrical conductivity of SiO_2 ceramics by 14 orders of magnitude; an increase in the resistance creep by two orders of magnitude was observed for Al_2O_3-based ceramics. Nanotubes impede or even exclude crack propagation (Fig. 12).

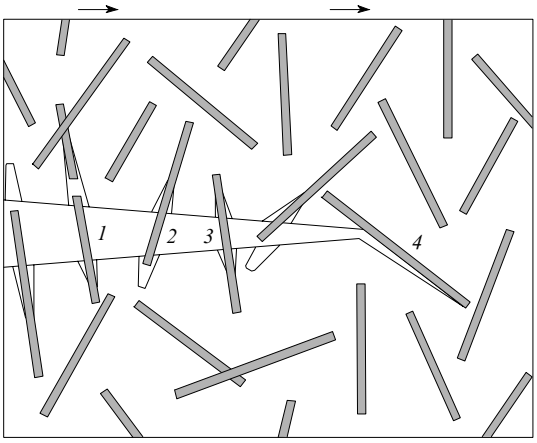


Figure 12. Schematics of ceramics hardening by nanotubes.
Hardening due to the energy spent (*1*) to break CNTs upon their drawing, (*2*) to break CNT–matrix bonds and (*3*) to extend the CNTs linking the crack walls; (*4*) deflection of a crack by a nanotube.
Arrows show the crack propagation direction.

CNT-based ceramic composites may have a fibre shape. In particular, SiC fibres containing multiwalled CNTs were described in the study.[243]

Glass-based composites are not widespread yet. Transparent CNT-containing SiO_2 glasses and glasses based on aluminoborosilicates, chalcogenides and metals have been synthesized. It was proposed to increase the tensile strength of glass fibre by coating it with a thin layer of epoxy resin containing 0.3 mass % CNTs.

The interest in carbon nanomaterials as tools for improving the quality of concrete arose not long ago: the first study[244] with an analysis of the problem and experimental results on CNTs was published in 2003. Then the research and developments in this field were significantly intensified. Detailed reviews[245–247] of the studies devoted to the influence of CNT additives on the concrete characteristics were published, as well as many original works (see, *e.g.*, Refs. 248–255).

The porous structure of the aggregate determines the low tensile and bending strength of concrete, as well as low toughness of cement concrete. Along with macro- and microdefects, concrete contains nanodefects, which are not affected by conventional fillers. CNTs act in a different way: their introduction, even in very small amounts (< 0.1 mass %), may increase the crack resistance and strength of concrete and reduce its shrinkage. Introduction of CNTs with a concentration as low as 0.022 mass % positively affects the concrete properties.[245]

Several techniques for introducing CNTs into concrete have been described. The basic ones can be combined into two groups: (i) techniques using make-up water (or superplasticisers) and (ii) techniques based on growth of CNTs on cement or cement components. Nanotubes are dispersed in water using surfactants, polymer dispersants (water-soluble polycarboxylates, polyacrylic acid, melamine-formaldehyde, *etc.*), polyelectrolytes, chemical modification by a mixture of acids and long-term ultrasonic treatment.

CNTs affect most significantly the properties of foam concrete. Introduction of 0.05% CNT results in reduced concrete density, increased compression strength, decreased thermal conductivity, smaller size of pores and their more uniform structure. CNT additives reduce the porosity of conventional concrete.[256]

Introduction of CNTs with superplasticisers is often the most efficient technique. For example, addition of multiwalled CNTs (produced by Graphistrength™, France) in amount of 0.006% of the mass of cement with an aqueous solution of Poliplast SP-1 superplasticiser increases the bending and compression strengths of concrete by 38.8% and 96.8%, respectively.[257]

CNT growth directly on cement is less efficient because of the change in its phase composition and structure at the synthesis temperature. Nanotubes grown on individual cement components (tetracalcic aluminoferrite, fired kaolin, or SiO_2 with additives of metal salts) are hydrophobic, and this fact negatively affects the behaviour of the system. However, the concrete properties were improved to a certain extent in some studies.[251,258,259] Introduction of surfactant makes the CNT distribution more uniform; it is also favourable for the mechanical characteristics of concrete.[260]

It was experimentally shown that there is an optimal concentration of introduced CNTs, above which the mechanical characteristics of concrete are not improved but deteriorate.

Along with CNTs, relatively inexpensive vapour-phase carbon fibres, produced in the United States, have been tested as additives. They have a conical structure of graphene layers, a diameter of 60–200 nm, a length of 30–100 μm and a specific surface area of 50–60 $m^2\ g^{-1}$ (Ref. 261).

Addition of Pyrograf III vapour-phase carbon fibres (in amount of 0.2 mass %) to portland cement with polycarboxylate-based Glenium 7500 plasticiser increased the cement tensile strength by 22%; simultaneous introduction of foamed silica gel increased this characteristic by 26%.[262] It was stated[262] that the strengthening effect of vapour-

phase carbon fibres exceeds that of thin CNTs (with a diameter of 9.5 nm, a length of 1.5 μm and a specific surface area of 250–300 $m^2 g^{-1}$) because of their larger aspect ratio.

Some researchers explain the strengthening effect of CNTs by the structurization of matrix layers near the CNT surface.[263] It is also suggested that chemical bonds are formed between OH groups on the CNT surface and the C–S–H phase of cement[250] and between the surface CO_2H groups and calcium hydrosilicates[249] or water molecules.[252]

One might suggest that there are several general mechanisms of the effect of additives of different carbon nanoparticles. The likely structurization of matrix by graphene planes occurs due to the influence of π electrons of the carbon atoms in these planes on the electrostatic interactions in the gel of hydrated calcium silicates. The strength of this interaction depends on the concentration and properties of surface functional groups. The other mechanism is related to the change in the rheological properties of surfactant; aqueous dispersion with surfactant; make-up water; and, finally, the cement solution. In all cases conditions for enhanced hydration of cement components and formation of denser hydration products may arise.

Introduction of CNTs into a concrete coating allows one (in principle) to monitor structural damage, perform remote sensing of road surface and remove ice from the latter by heating. Here, an important requirement is to provide conditions for uniform dispersion of nanotubes, which cannot always be done. That is why numerous attempts to introduce CNTs into building mixtures were no success, and the state of art in this area of materials science is estimated to be in its infancy.

Metal composites of CNTs with Ag, Mg, Al, Ti, Sb, Co and Ni; metal glasses $Fe_{82}P_{18}$; and Al–Si, Mg–Al, Sn–Sb, Sn–Co, Ti–V alloys (the latter composite is used to accumulate hydrogen) were described.[264]

Monograph,[265] devoted to CNT composites with metals, general review,[266] and particular review[267] on magnesium nanocomposites have been published. However, a majority of studies were devoted to copper-based composites (see, *e.g.*, Refs 268–270). The yield stress and Young's modulus of these composites can be increased two- to threefold. Addition of 1 vol.% multiwalled CNTs to a copper powder subjected to equichannel angular pressing resulted in an increase in the sample hardness by a factor of more than two after eight cycles.[271] Small CNT additives strengthen magnesium and sharply increase its corrosion durability in salty water. Introduction of 10 mass % CNTs into aluminium-based composite obtained by hot pressing increases its microhardness from 30 to 58 kg mm^{-2}.

Composites with metals exhibit tribological properties;[272] they are characterized by small coefficients of thermal expansion[273] and low densities. Composites are obtained by methods of powder metallurgy, casting under pressure, or casting with mixing, as well as using plane shock waves, thermal sputtering, decoration of CNTs with metals and subsequent compaction. Methods of thermal and plasma deposition are also applied.[274, 275] Decoration can be performed electrochemically, by reducing metal salts with organic and inorganic reagents and (in some cases) by reducing salts using CNTs or a substrate with a CNT array on its surface. Electrodeposition is applied to form Ni–CNT composite coatings.[276]

Unprecedently high strengthening effect was obtained by chemical modification of CNTs (functionalization, ion exchange with the aid of salts, reduction of metals) and subsequent pressing.

Layered composites were prepared by rolling foil assemblies.[277]

Currently, unique composite materials consisting of only carbon are developed. Examples are films composed of CNTs and 'nanohorn' aggregates,[278] CNTs and graphene films,[279] CNTs inserted between graphene layers,[280] CNT forest grown on a graphene film,[281] forest grown between graphene layers,[282] CNFs formed on graphene strips,[283] CNTs located in pores of thermally expanded graphite,[284] graphite films on a forest,[285] single-walled CNTs on the surface of a forest of multiwalled CNTs,[286] pressed and sintered composite consisting of carbon microspheres and CNTs,[287] foamed composite consisting of CNT dispersion with cellulose (carbonized),[288] *etc.*

This group of materials includes composites of carbon aerogel with CNTs[289–292] and elastic composite with a density of ~10 mg cm^{-3}, whose volume can be reversibly reduced by 80% under compression.[293] The latter composite was obtained from a CNT dispersion in the presence of resorcinol and formaldehyde by drying in supercritical CO_2 and pyrolysis at 1050 °C. These materials are promising for supercapacitor electrodes. A more complex material was designed by growing CNTs on carbon microfibre paper, impregnating the product with polyacrylonitrile solution in dimethylformamide, drying and carbonizing.[294]

The attempts to use sulfur/CNT composite for electrodes of lithium–sulfur batteries were no success because of the fast decrease in capacitance upon cycling.[295]

VIII. Hybrid materials with carbon nanotubes

Along with composites of 'classical' type, hybrid composites (containing, *e.g.*, three components: fibres, CNTs and binder) are also intensively studied and developed. These materials can be produced using polymer, ceramic, or carbon fibre, as well as glass fibre. For example, application of hybrid composites allows one to reduce the civil airframe weight by more than 50%.

CNTs can be introduced in several ways: directly into the fibre bulk,[296, 297] on the fibre surface (into the finishing material),[298–301] on the surface of a ready fibre cloth,[302, 303] into the binder,[304–307] and in the form of a separate interlayer between fibre or cloth layers.[308] Nanopaper[309] or CNT forest sheets were used as interlayers. Two or more ways of introducing CNTs can be used simultaneously. The peculiar hybrid material — forest with polydimethylsiloxane interlayers — was described.[310]

Reviews on hybrid layered CNT-containing composites[311] and on introduction of CNTs into layered composites obtained by vacuum moulding[312] were published. A particular place is occupied by composites with nanosized layers.[311] CNT interlayers can play a role of a peculiar 'Velcro', which rigidly connects layers and increases the layered-composite strength (Fig. 13).[313]

Each of the above-described ways has advantages and drawbacks. For example, introduction of CNTs into the bulk of polymer fibres calls for oriented tube packing (coaxially with the fibre), which complicates fibre formation. To grow CNTs on the fibre surface using hydrocarbon pyrolysis, it is necessary to perform preliminary deposition of catalyst; however, this operation reduces the fibre

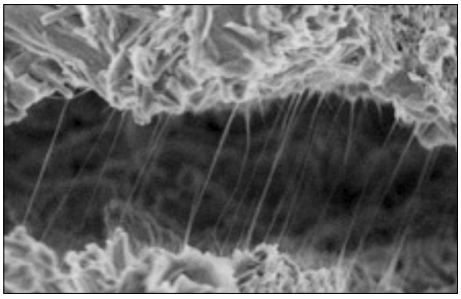
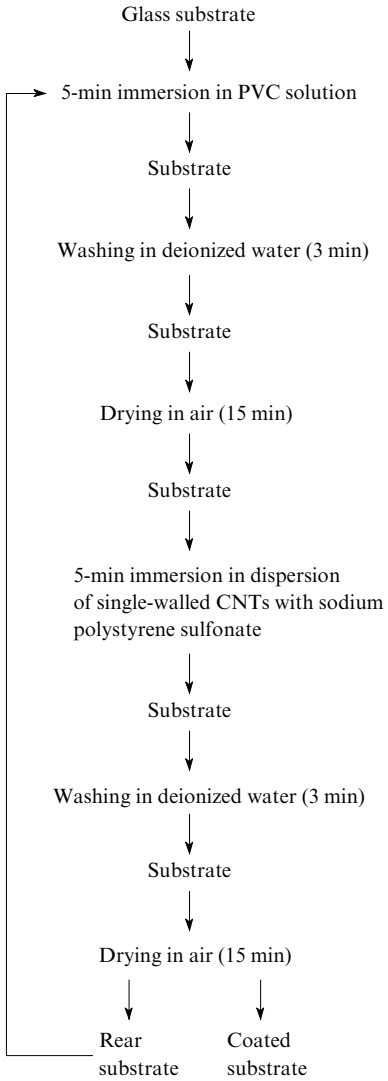


Figure 13. Strengthening effect of CNT forest interlayer in prepregs.[313]

Scheme 2



strength. Nevertheless, hybrid CNT-containing materials‡ are considered as promising, and Zyvex corporation (the United States) has been using hybrid composites with 0.5 mass % CNTs in production of light motor boats and yachts. Zyvex has also released a CNT concentrate in epoxy resin and CNT-containing adhesive (Epovex). The strength of CNT-containing prepregs is 30% – 50% higher than that of conventional prepregs. Nanocyl company (Belgium) also produces CNT-containing resin and fibres.

Hybrid CNT-containing nanocomposites may have damage sensoring properties[315] and be used for self-diagnostics.[316] It was proposed to use thin films obtained by layer-by-layer deposition of polyelectrolytes in strain and corrosion sensors.[317] In particular, Scheme 2 shows the stages of forming alternating CNT-containing layers of polyvinyl alcohol and sodium polystyrene sulfonate.

Hybrid nanocomposites are considered to be those based on polymers with two types of fillers. The latter, along with CNTs, can be clay or graphite nanoparticles,[318] stainless steel fibres,[319] *etc.*

The electrical conductivity and wetting angle of hybrid material — CNT nanopaper of shish-kebab type (nanotubes decorated by periodically arranged associates of polyethylene crystals) — can be controlled by changing the CNT concentration from 13 mass % to 70 mass %.[320]

IX. Biocomposites with carbon nanotubes

Since CNTs have nanoscale sizes, they can affect significantly biological objects. CNT biocomposites are very promising for applications in this field;[321] however, as was noted in review,[322] this research is at its infancy. The behaviour of CNT materials in biological media differs from the behaviour of individual nanotubes.

Medical and biological applications of CNTs and CNT materials are as follows: design of biosensors, drug delivery tools to patient organs, biological tags,[323, 324] and materials for prosthetics. Unoxidized, nonfunctionalized, and standardized CNTs are preferred in biological applications.

Biocomposites are materials for biological applications and materials containing substances of biological origin. CNT biocomposites with polymer and inorganic matrices have been developed. Materials for bone cement (based on polymethyl methacrylate with up to 10 mass % multiwalled CNTs) and bone implants (based on hydroxyapatite[325] or hydroxyapatite and polymethyl methacrylate with CNT additives) were proposed. Active interest is shown in CNT nanopaper for growing muscular and bone tissues, retina and epithelial cells of the eye and neuron networks.[326–334] They include, in particular, composite with collagen[335, 336] and composite with a small amount of chitosan.[337] Strong composite coatings with CNT-functionalized chitosan were obtained by electrodeposition on a steel spring.[338] Chitosan-based composites have some other applications.[339]

Antibacterial porous composite containing CNTs with polyvinylpyrrolidone–iodine complex coating was proposed to heal wounds and reconstruct nerve tissues.[340]

Biofunctional nanocomposites (see, *e.g.*, Ref. 341) and biosensors[342–344] have been developed. CNTs modified by proteins, peptides, and DNA chains were described. Biomolecules in these composites can be located not only on the external CNT surface but also in the internal cavities of open-end nanotubes. Functionalization of CNTs by bilayer lipids is considered to be the main application of membrane proteins in nanodevices.

A composite with natural biopolymer for electromechanical actuator has been elaborated,[345] and the development of smart biological CNT-containing materials is under way.[346]

‡ In some reviews hybrid composites containing fibres and CNTs are referred to as hierarchical (see, *e.g.*, Ref. 314).

X. Dispersions and solutions of carbon nanotubes

In materials science, dispersions and solutions are not considered as materials. However, the great role of CNT dispersions in the producion of materials and possibilities of the use of particular CNT dispersions along with mateirals (for example, as laser radiation power limiting means or heat-conducting media) justify the inclusion of their brief characterization in this review.

Carbon cannot form solutions in any form if its particles are not modified. According to the modification way, three types of CNT dispersions in water and organic solvents are distinguished:

— dispersions containing CNTs without chemical bonds with the dispersant;

— dispersions containing CNTs with covalently attached functional groups;

— dispersions with protonated CNTs and CNT 'salts'.

In turn, noncovalent solubilization can be obtained in different ways: using surfactants, linear polymers, polyaromatic compounds, liquid crystals, or biomolecules.[53, 347–352] Reviews on the chemical modification and dispersion of CNTs have been published, as well as short review[353] on the use of microwave activation (the importance of which constantly increases in the case of CNTs) in synthesis of nanomaterials.

The first studies on dispersion of CNTs with covalently bound groups were performed at Rice University (Houston) and Universities of Kentucky and Louisville (the United States).[354–357] CNTs can be functionalized in the simplest way by heating them in a mixture of concentrated sulfuric and nitric acids, as a result of which carboxyl, hydroxyl, carbonyl and other (in smaller amounts) oxygen-containing groups are formed. Then esterification, amidation, or other reactions can be performed; the total list of covalent functionalization versions is rather long.

Superacids protonate CNTs and make it possible to reach relatively high concentrations of nanotubes in solutions.[142, 358] Solutions in chlorosulfonic acid can also be used.[359] CNT salts are obtained using solutions of alkali metals in liquid NH_3 (see, *e.g.*, Ref. 360).

Viscous liquids with rather high CNT concentrations have been selected in the case of polyethylene glycol[361] (to 20 mass % CNT) or silicone (85 mass % CNT).[362]

Dispersions and lubricants containing CNTs and characterized by a relatively high thermal conductivity are peculiar media; they are used to eliminate air gaps between contacting surfaces and reduce the thermal resistance in construction parts.

XI. Conclusion

We share the competent opinion stated in review,[14] according to which the main problems in the field of CNTs are as follows:

— mass production of inexpensive CNTs;

— development of selective methods for fabricating CNTs with a certain structure and properties;

— strictly localized deposition of clearly oriented CNTs on substrates;

— elucidation of the mechanism of CNT formation.

However, the list of these problems should be supplemented by at least one more: fabrication of CNT and CNT-containing materials, especially so that the authors of the aforementioned review considered the state of the art with the fabrication of CNT macrofibres and arrays of vertically and horizontally arranged CNTs as one of the most important subjects. The situation is hindered by the fact that the properties exhibited by materials at the molecular level can hardly be reproduced in macroscopic materials because of the presence of defects, weak intermolecular bonds and foreign inclusions. Nevertheless, the range of application of CNT materials are being constantly expanded.

Since the pyrolytic methods of CNT formation displaced all others, the comparative estimation of the three basic versions of these methods, reported in review[14] should be supplemented (Table 1).

The developments of the latest years showed that the aforementioned 'supergrowth', which was described for the first time in 2004,[38] has a good scalability, due to which one can obtain high-quality long CNTs in a high yield, as well as three-dimensional structures. In particular, the principle of continuous process was described; it is currently being improved.[363] The CNT yield per gramme of the catalyst is several orders of magnitude higher than that obtained by other methods, and the CNT purity reaches 99.5 mass %.[41] The results of studying the CNT growth on ceramic balls[45, 364–366] also demonstrate some possibilities of wide scaling.

The techniques of gas-flow-induced directed growth of long CNTs[58–65] have certain advantages over conventional pyrolytic processes. These methods (which also make it possible to control the CNT diameter and length) are characterized by a high specific catalyst output, do not call for time-consuming purification from catalyst and can be scaled. However, the specific output (product weight per unit time per reactor unit volume and unit area) of these methods is much lower than that of the supergrowth processes. Currently, specifically supergrowth opens new prospects of efficient production of CNT materials and CNT-containing nanocomposites.

A number of other materials and many methods of their production, including those having commercial prospects, remained beyond the scope of this review. For example, the internal CNT cavity can be filled by various substances to provide material with new properties.[367] The number of types of CNT materials constantly increases due to the use of decoration and filling.[368–371] Polymer nanocomposites may contain CNTs decorated by inorganic materials, *e.g.*,

Table 1. Qualitative characteristics of CNT mass production methods.[14]

Method	Temperature	Scalability	Efficiency	CNT purity	CNT quality	Packing
With flying catalyst	high	high	high	high	very high	unknown
With fluidized bed	medium	very high	"	poor	high	disordered
Supergrowth	"	–	very high	very high	"	ordered

ZrO_2.[372] Nanocomposites with CNTs, containing simultaneously metal oxides and metals, have been developed.

Many of the materials and methods for their production that were considered in this review should also be described much more thoroughly. CNT materials and CNT-containing nanocomposites have certain advantages over conventional commercial materials; therefore, the studies on CNT applications in various materials are in rapid progress.

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References

1. P J F Harris *Int. Mater. Rev.* **49** 31 (2004)
2. H G Chae, S Kumar, in *Nanoengineering of Structural, Functional and Smart Materials* (Eds M Schulz, A Kelkar, M Sundaresan) (Boka Raton, FL: CRC Press, 2005) p. 286
3. F Du, K I Winey, in *Nanomaterials Handbook* (Ed. Yu Gogotsi) (Boka Raton, FL, London, New York: CRC Press, Taylor Francis, 2006) p. 565
4. F Hussain, M Hojjati, M Okamoto, R E Gorga *J. Compos. Mater.* **40** 1511 (2006)
5. S Bal, S S Samal *Bull. Mater. Sci.* **30** 379 (2007)
6. T Ozel, A Gaur, J A Rogers, M Shim *Nano Lett.* **5** 905 (2005)
7. J Liu, M C Hersam *MRS Bull.* **35** 315 (2010)
8. J Posseckardt, Y Battie, R Fleurier, J-S Lauret, A Loiseau, O Jost, M Mertig *Phys. Status Solidi B* **247** 2687 (2010)
9. E S Snow, J P Novak, P M Campbell, D Park *Appl. Phys. Lett.* **82** 2145 (2003)
10. K Bradley, J-C P Gabriel, G Grüner *Nano Lett.* **3** 1353 (2003)
11. T Takenobu, T Takahashi, T Kanabara, K Tsukagoshi, Y Aoyagi, Y Iwasa *Appl. Phys. Lett.* **88** 33511 (2006)
12. O Zhou, H Shimoda, B Gao, S Oh, L Fleming, G Yue *Acc. Chem. Res.* **35** 1045 (2002)
13. F Wei, Q Zhang, W Z Qian, G H Xu, R Xiang, Q Wen, Y Wang, G H Luo *New Carbon Mater.* **22** 271 (2007)
14. E Joselevich, H Dai, J Liu, K Hata, A H Windle, in *Carbon Nanotubes (Top. Appl. Phys.)* Vol. 111 (Eds A Jorio, G Dresselhaus, M S Dresselhaus) (Berlin, Heidelberg: Springer, 2008) p. 101
15. P Eklund P Ajayan, R Blackmon, A J Hart, J Kong, B Pradhan, A Rao, A Rinzler *International Assessment on Research and Development of Carbon Nanotube Manufacturing and Application. WTEC Panel Rer.* (Baltimore: World Technology Evaluation Center, 2007)
16. E G Rakov *Vse Materialy. Entsiklop. Sprav.* (10) 14 (2011)
17. A Oberlin, M Endo *J. Cryst. Growth* **32** 335 (1976)
18. S Iijima *Nature (London)* **354** 56 (1991)
19. S Iijima, T Ichihashi *Nature (London)* **363** 603 (1993)
20. N M Builova, S P Yashukova *Nauch.-Tekhn. Inform., Ser. 2* (12) 24 (2007)
21. W Marx, A Barth *Phys. Status Solidi B* **245** 2347 (2008)
22. W Marx, A Barth, in *Carbon Nanotube* (Online Ed.) (Ed. J M Marulanda) (Vienna: InTech., 2010) p. 1
23. M S Dresselhaus *ACS Nano* **4** 4344 (2010)
24. M Endo, T Hayashi, Y A Kim, H Muramatsu *Jpn. J. Appl. Phys.* **45** 4883 (2006)
25. E G Rakov, I V Baronin *Nanotekhnika* (3) 3 (2007)
26. *Production and Application of Carbon Nanotubes, Carbon Nanofibers, Fullerenes, Graphene and Nanodiamonds: a Global Technology Survey and Market Analysis* (Stamford, CT: Innovative Research and Production Inc., 2011)
27. *Global Carbon Nanotubes Market 2010–2014* (Naperville, IL: Infiniti Research Lim., 2011)
28. *Global Carbon Nanotubes Market — SWCNTs, MWCNTs, Technology Applications, Trends and Outlook (2011–2016)* (Dallas, TX: Market Publ., 2011)
29. *World Market for Nanotechnology: Applications, Markets and Companies* (Albany, NY: Future Markets, 2011)
30. E G Rakov *Nanotrubki i Fullereny* (Nanotubes and Fullerenes) (Moscow: Universitetskaya Kniga, Logos, 2006)
31. E G Rakov *Khim. Tekhnol.* (10) 2 (2003) [a]
32. K B K Teo, C Singh, M Chhowalla, W I Milne, in *Encyclopedia of Nanoscience and Nanotechnology Fullerenes.* Vol. 1 (Online Ed.) (Ed. H S Nalwa) (American Scientific Publ., 2004) p. 665
33. M Meyyappan *Carbon Nanotube: Science and Applications* (Boka Raton, FL: CRC Press, 2004)
34. E G Rakov *Ros. Khim. Zh.* **48** (5) 12 (2004) [b]
35. E G Rakov *Russ. Chem. Rev.* **76** 1 (2007)
36. E G Rakov *Ros. Nanotekhnol.* **3** (9–10) 63 (2008) [c]
37. V M Sivakumar, A R Mohamed, A Z Abdullah, S-P Chai *J. Nanomater.* 395191 (2010)
38. K Hata, D N Futaba, K Mizuno, M Yumura, S Iijima *Science* **306** 1362 (2004)
39. D N Futaba, K Hata, T Yamada, K Mizuno, M Yumura, S Iijima *Phys. Rev. Lett.* **95** 056104 (2005)
40. D N Futaba, K Hata, T Namai, T Yamada, K Mizuno, Y Hayamizu, M Yumura, S Iijima *J. Phys. Chem. B* **110** 8035 (2006)
41. S Yasuda, T Hiraoka, D N Futaba, T Yamada, M Yumura, K Hata *Nano Lett.* **9** 769 (2009)
42. K Hata *AIST Today* (41) 9 (2011)
43. Q Zhang, M Zhao, J Huang, Y Liu, Y Wang, W Qian *Carbon* **47** 2600 (2009)
44. Q Zhang, M-Q Zhao, J-Q Huang, J-Q Nie, F Wei *Carbon* **48** 1196 (2010)
45. D Y Kim, H Sugime, K Hasegawa, T Osawa, S Noda *Carbon* **49** 1972 (2011)
46. S A Zhdanok, A V Krauklis, I F Buyakov, V M Volzhankin, K O Borisevich, P P Samtsov *Inzh.-Fiz. Zh.* **4** 617 (2008) [d]
47. A G Tkachev, I V Zolotukhin *Apparatura i Metody Sinteza Tverdotel'nykh Struktur* (Equipment and Methods of Synthesis of Solid-State Structures) (Moscow: Mashinostroenie, 2007)
48. C Z Wu, W Luo, B Ning, Y Xie *Chin. Sci. Bull.* **54** 1894 (2009)
49. C P Marsh, P B Stynoski, T A Carlson, C Arnett, B Newcomb, M S Strano, C S Welch *Carbon* **49** 1235 (2011)
50. G Kickelbick, in *Hybrid Materials. Synthesis, Characterization, and Applications* (Ed. G Kickelbick) (Weinheim: Wiley, 2007) p. 1
51. K T Lau, D Hui *Composites, B* **33** 263 (2002)
52. P M Ajayan, O Stephan, C Colliex, D Trauth *Science* **265** 1212 (1994)
53. N Karousis, N Tagmatarchis, D Tasis *Chem. Rev.* **110** 5366 (2010)
54. M B Bryning, D E Milkie, M F Islam, L A Hough, J M Kikawa, A G Yodh *Adv. Mater.* **19** 661 (2007)
55. J Zou, J Liu, A S Karakoti, A Kumar, D Joung, Q Li, S I Khondaker, S Seal, L Zhai *ACS Nano* **4** 7293 (2010)
56. S-M Kwon, H-S Kim, H-J Jin *Polymer* **50** 2786 (2009)
57. M Xu, D N Futaba, T Yamada, M Yumura, K Hata *Science* **330** 1364 (2010)
58. S M Huang, X Y Cai, J Liu *J. Am. Chem. Soc.* **125** 5636 (2003)
59. S M Huang, Q Fu, L An, J Liu *Phys. Chem. Chem. Phys.* **6** 1077 (2004)
60. S D Li, Z Yu, C Rutherglen, P J Burke *Nano Lett.* **4** 2003 (2004)
61. Z Yu, S D Li, P J Burke *Chem. Mater.* **16** 3414 (2004)
62. B H Hong, J Y Lee, T Beetz, Y M Zhu, P Kim, K S Kim *J. Am. Chem. Soc.* **127** 15336 (2005)

63. H Liu, D Tagake, S Chiashi, Y Homma *Nanotechnology* **20** 345604 (2009)
64. X Wang, Q Li, J Xie, Z Jin, J Wang, Y Li, K Jiang, S Fan *Nano Lett.* **9** 3137 (2009)
65. Y Li, R Cui, L Ding, Y Liu, W Zhou, Y Zhang, Z Jin, F Peng, J Liu *Adv. Mater.* **22** 1508 (2010)
66. M M Shulaker, H Wei, N Patil, J Provine, H-Y Chen, H-S P Wong, S Mitra *Nano Lett.* **11** 1881 (2011)
67. E Dervishi, Z Li, F Watanabe, V Saini, A R Biris, Y Xu, A S Biris *Diamond Relat. Mater.* **19** 67 (2010)
68. W Zhou, L Ding, S Yang, J Liu *ACS Nano* **5** 3849 (2011)
69. C Wang, K Ryu, L G De Arco, A Badmaev, J Zhang, X Lin, Y Che, C Zhou *Nano Res.* **3** 831 (2010)
70. S Takada, T Nakai, T Thurakitseree, J Shiomi, S Maruyama, H Takagi, M Shuzo, J-J Delaunau, I Yamada *IEEJ Trans.* **130** 207 (2010)
71. L Hu, D S Hecht, G Grüner *Chem. Rev.* **110** 5790 (2010)
72. H Liu, D Takagi, S Chiashi, Y Homma *ACS Nano* **4** 933 (2010)
73. M A Meitl, Y Zhou, A Gaur, S Jeon, M L Usrey, M S Strano, J A Rogers *Nano Lett.* **4** 1643 (2004)
74. A Allen, A Cannon, J Lee, W P King, S Graham *J. Micromech. Microeng.* **16** 2722 (2006)
75. A C Allen, E Sunden, A Cannon, S Graham, W King *Appl. Phys. Lett.* **88** 083112 (2006)
76. Y Chai, J Gong, K Zhang, P C H Chan, M M F Yuen *Nanotechnology* **18** 355709 (2007)
77. D R Hines, S Mezhenny, M Breban, E D Williams, V W Ballaroto, G Esen, A Southard, M S Fuhrer *Appl. Phys. Lett.* **86** 163101 (2005)
78. H Huang, C Liu, Y Wu, S Fan *Adv. Mater.* **17** 1652 (2005)
79. H Jiang, L Zhu, K-S Moon, C P Wong *Nanotechnology* **18** 125203 (2007)
80. S Li, Y Yan, N Liu, M B Chan-Park, Q Zhang *Small* **3** 616 (2007)
81. S M L Nai, M Gupta, J Wei *Int. J. Nanosci.* **4** 423 (2005)
82. E Sunden, J K Moon, C P Wong, W P King, S Graham *J. Vac. Sci. Technol., B* **24** 1947 (2009)
83. T Wang, B Carlberg, M Jonsson, G-H Jeong, E E B Campbell, J Liu *Appl. Phys. Lett.* **91** 093123 (2007)
84. L Zhu, Y Sun, D W Hess, C-P Wong *Nano Lett.* **6** 243 (2006)
85. A Kaskela, A G Nasibulin, M Y Timmermans, B Aitchison, A Papadimitrakos, Y Tian, Z Zhu, H Jiang, D P Brown, A Zakhidov, E I Kauppinen *Nano Lett* **10** 4349 (2010)
86. R L D Whitby, T Fukuda, T Maekawa, S L James, S V Mikhalovsky *Carbon* **46** 949 (2008)
87. M Endo, H Muramatsu, T Hayashi, Y A Kim, M Terrones, M S Dresselhaus *Nature (London)* **433** 476 (2005)
88. Y A Kim, H Muramatsu, T Hayashi, M Endo, M Terrones, M S Dresselhaus *Chem. Vap. Deposit.* **12** 327 (2006)
89. H Muramatsu, T Hayashi, Y A Kim, D Shimamoto, Y J Kim, K Tantrakam, M Endo, M Terrones, M S Dresselhaus *Chem. Phys. Lett.* **414** 444 (2005)
90. B Wang, Y Ma, N Li, Y Wu, F Li, Y Chen *Adv. Mater.* **22** 3067 (2010)
91. K Liu, W Ren, D W Wang, C G Chen, S Pei, B Liu, F Li, H Cong, Ch Liu, H M Cheng *ACS Nano* **3** 707 (2009)
92. S F A Acquah, D N Ventura, H W Kroto *Electronic Properties of Carbon Nanotubes* (Ed. J M Naruland) (Vienna: InTech., 2011)
93. S T Mostafavi, M R Mehrnia, A M Rashidi *Desalination* **238** 271 (2009)
94. L F Dumée, K Sears, J Schütz, N Finn, C Huynh, S Hawkins, M Duke, S Gray *J. Membr. Sci.* **351** 36 (2010)
95. U Vohrer, I Kolaric, M H Hague, S Roth, U Detlaff-Weglikowska *Carbon* **42** 1159 (2004)
96. A I Kirillov, A M Obyedkov, V A Yegorov, G A Domrachev, B S Kaverin, T I Lopatina, S A Gusev, A D Mansfeld *Nanotekhnika* (1) 72 (2011)
97. M Kaempgen, G S Duesberg, S Roth *Appl. Surf. Sci.* **252** 425 (2005)
98. M-S Jung, T-L Choi, W-J Joo, J-Y Kim, I-T Han, J M Kim *Synth. Met.* **157** 997 (2007)
99. A A Green, M C Hersam *Nano Lett.* **8** 1417 (2008)
100. H Gu, T M Swager *Adv. Mater.* **20** 4433 (2008)
101. H Zhu, B Wei *J. Mater. Sci. Technol.* **24** 447 (2008)
102. Q Cao, H-s Kim, N Pimparkar, J P Kulkarni, C Wang, M Shim, K Roy, M A Alam, J A Rogers *Nature (London)* **454** 495 (2008)
103. H-Z Geng, D S Lee, K K Kim, G H Han, H K Park, Y H Lee *Chem. Phys. Lett.* **455** 275 (2008)
104. Q Cao, J A Rogers *Adv. Mater.* **21** 29 (2009)
105. E M Doherty, S De, P E Lyons, A Shmeliov, P N Nirmalraj, V Scardaci, J Joimel, W J Blau, J J Boland, J N Coleman *Carbon* **47** 2466 (2009)
106. A Southard, V Sangwan, J Cheng, E D Williams, M S Fuhrer *Org. Electron.* **10** 1556 (2009)
107. J W Jo, J W Jung, J U Lee, W H Jo *ACS Nano* **4** 5382 (2010)
108. V Scardaci, R Coul, J N Coleman *Appl. Phys. Lett.* **97** 023114 (2010)
109. H Okimoto, T Takenobu, K Yanagi, Y Miyata, H Shimotani, H Kataura, Y Iwasa *Adv. Mater.* **22** 3981 (2010)
110. J Opatkiewicz, M C LeMieux, Z Bao *ACS Nano* **4** 2975 (2010)
111. G Tang, X Zhang, S Yang, V Derycke, J-J Benattar *Small* **6** 1488 (2010)
112. F Wang, M E Itkis, R C Haddon *Nano Lett.* **10** 937 (2010)
113. H S Mandal, A Ward, X S Tang *J. Nanosci. Nanotechnol.* **11** 3265 (2011)
114. Q Wang, H Moriyama *Carbon Nanotubes — Synthesis Characterization Applications* (Online Ed.) (Ed. S Yellampalli) (Vienna: InTech., 2011)
115. J van de Lagemaat, T M Barnes, G Rumbles, S E Shaheen, T J Coutts, C Weeks, I Levitsky, J Peltola, P Glatkowski *Appl. Phys. Lett.* **88** 233503 (2006)
116. *Indium: Global Industry Markets and Outlook* (9th Ed.) (London: Roskill Inform. Serv., 2010)
117. M Engel, J P Small, M Steiner, M Freitag, A A Green, M C Hersam, Ph Avouris *ACS Nano* **2** 2445 (2008)
118. C M Trottier, P Glatkowsky, P Wallis, J Luo *J. Soc. Inf. Disp.* **13** 759 (2005)
119. B Dan, G C Irvin, M Pasquali *ACS Nano* **3** 835 (2009)
120. B B Parekh, G Fanchini, G Eda, M Chhowalla *Appl. Phys. Lett.* **90** 121913 (2007)
121. Y Zhao, J Wei1, R Vajtai1, P M Ajayan, E V Barrera *Sci. Rep.* **83** 1 (2011)
122. M A Contreras, T Barnes, J van de Lagemaat, G Rumbles, T J Coutts, C Weeks, P Glatkowski, I Levitsky, J Peltola, D A Britz *J. Phys. Chem., C* **111** 14045 (2007)
123. S W Lee, N Yabuuchi, B M Gallant, S Chen, B-S Kim, P T Hammond, Y Shao-Horn *Nat. Nanotechnol.* **5** 531 (2010)
124. Y Wang, C-A Di, Y Liu, H Kajiura, S Ye, L Cao, D Wei, H Zhang, Y Li, K Noda *Adv. Mater.* **20** 4442 (2008)
125. I Kang, Y T Heung, J H Kim, J W Lee, R Gollapudi, S Subramanian, S Narasimhadevara, D Hurd, G R Krikera, V Shanov, M J Schulz, D Shi, J Boerio, S Mall, M Ruggers-Wren *Composites, B* **37** 387 (2006)
126. G Sun, Y Zhang, L Zheng *J. Nanomater.* **2012** 506209 (2012)
127. N Behabtu, M J Green, M Pasquali *Nano Today* **3** (5 – 6) 24 (2008)
128. T-W Chou, L Gao, E T Thostenson, Z Zhang, J-H Byun *Compos. Sci. Technol.* **70** 1 (2010)
129. Y-L Li, I A Kinloch, A H Windle *Science* **304** 276 (2004)
130. K Koziol, J Vilatela, A Moisala, M Motta, P Cunniff, M Sennett, A Windle *Science* **318** 1892 (2007)
131. K L Stano, K Koziol, M Pick, M S Motta, A Moisala, J J Vilatela, S Frasier, A H Windle *Int. J. Mater. Form.* **1** 59 (2008)

132. S Boncel, R M Sundaram, A H Windle, K K K Koziol *ACS Nano* **5** 9339 (2011)
133. X H Zhong, Y L Li, Y K Liu, X H Qiao, Y Feng, J Liang, J Jin, L Zhu, F Hou, J Y Li *Adv. Mater.* **22** 692 (2010)
134. L Zheng, X Zhang, Q Li, S B Chikkannanavar, Y Li, Y Zhao, X Liao, Q Jia, S K Doorn, D E Peterson, Y Zhu *Adv. Mater.* **19** 2567 (2007)
135. C Fang, J Zhao, J Jia, Z Zhang, X Zhang, Q Li *Appl. Phys. Lett.* **97** 181906 (2010)
136. S Ryu, Y Lee, J-W Hwang, S Hong, C Kim, T G Park, H Lee, S H Hong *Adv. Mater.*. **23** 1971 (2011)
137. Z Yang, X Sun, X Chen, Z Yong, G Xu, R He, Z An, Q Li, H Peng *J. Mater. Chem.* **21** 13772 (2011)
138. B Vigolo, A Penicaud, C Coulon, C Sauder, R Pailler, C Journet, P Bernier, P Poulin *Science* **290** 1331 (2000)
139. P Poulin, B Vigolo, P Launois *Carbon* **40** 1741 (2002)
140. Y Jia, X Li, P Li, K Wang, A Cao, J Wei, H Zhu, D Wu *Nanoscale Res. Lett.* **7** 137 (2012)
141. L M Ericson, H Fan, H Peng, V A Davis, W Zhou, J Sulpizio, Y Wang, R Booker, J Vavro, C Guthy, A N G Parra-Vasquez, M J Kim, S Ramesh, R K Saini, C Kittrell, G Lavin, H Schmidt, W W Adams, W E Billups, M Pasquali, W-F Hwang, R H Hauge, J E Fischer, R E Smalley *Science* **305** 1447 (2004)
142. V A Davis, A N-G Parra-Vasquez, M J Green, P K Rai, N Behabtu, V Prieto, R D Booker, J Schmidt, E Kesselman, W Zhou, H Fan, W W Adams, R H Hauge, J E Fischer, Y Cohen, Y Talmon, R E Smalley, M Pasquali *Nat. Nanotechnol.* **4** 830 (2009)
143. S Zhang, K K K Koziol, I A Kinloch, A H Windle *Small* **4** 1217 (2008)
144. D N Futaba, J Goto, S Yasuda, T Yamada, M Yumura, K Hata *Adv. Mater.* **21** 4811 (2009)
145. S Yasuda, D N Futaba, T Yamada, J Satou, A Shibuya, K Hata *ACS Nano* **3** 4264 (2009)
146. G O Ince, G,Demirel, K K Gleason, M C Demirel *Soft Matter* **6** 1635 (2010)
147. E Einarsson, Y Murakami, M Kadowaki, H M Duong, M Inoue, S Maruyama *Thermal Sci. Eng.* **14** 47 (2006)
148. M De Volder, S H Tawfick, S J Park, D Copic, Z Z Zhao, W Lu, A J Hart *Adv. Mater.* **22** 4384 (2010)
149. K Kempa, B Kimball, J Rybczynski, Z P Huang, P F Wu, D Steeves, M Sennett, M Giersig, D V G L N Rao, D L Carnahan, D Z Wang, J Y Lao, W Z Li, Z F Ren *Nano Lett.* **3** 13 (2003)
150. H Shi, J G Ok, H W Baac, L J Guo *Appl. Phys. Lett.* **99** 211103 (2011)
151. L K Randeniya, A Bendavid, P J Martin, C-D Tran *Small* **6** 1806 (2010)
152. C L Pint, Y Q Xu, M Pasquali, R H Hauge *ACS Nano* **2** 1871 (2008)
153. S Tawfick, K O'Brien, A J Hart *Small* **5** 2467 (2009)
154. M Yu, H H Funke, J L Falconer, R D Noble *Nano Lett.* **9** 225 (2009)
155. K L Jiang, Q Q Li, S S Fan *Nature (London)* **419** 801 (2002)
156. M Zhang, K R Atkinson, R H Baughman *Science* **306** 1358 (2004)
157. K Liu, Y Sun, X Lin, R Zhou, J Wang, S Fan, K Jiang *ACS Nano* **4** 5827 (2010)
158. K Liu, Y Sun, R Zhou, H Zhu, J Wang, L Liu, S Fan, K Jiang *Nanotechnology* **21** 045708 (2010)
159. X Zhang, Q Li, T G Holesinger, P A Arendt, J Huang, P D Kirven, T G Clapp, R F De Paula, X Liao, Y Zhao, L Zheng, D E Peterson, Y Zhu *Adv. Mater.* **19** 4198 (2007)
160. Y Zhang, G Zou, S K Doorn, H Htoon, L Stan, M E Hawley, C J Sheehan, Y Zhu, Q Jia *ACS Nano* **3** 2157 (2009)
161. J Jia, J Zhao, G Xu, J Di, Z Yong, Y Tao, C Fang, Z Zhang, X Zhang, L Zheng, Q Li *Carbon* **49** 1333 (2011)
162. M D Lima, S Fang, X Lepró, C Lewis, R Ovalle-Robles, J Carretero-Gonzáles, E Cartillo-Martínez, M E Kozlov, J Oh, N Rawat, C S Haines, M H Hague, V Aare, S Staugnton, A A Zakhidov, R N Baughman *Science* **311** 51 (2011)
163. X Lepro, M D Lima, R H Baughman *Carbon* **48** 3621 (2010)
164. A E Aliev, J Oh, M E Kozlov, A A Kuznetsov, S Fang, A F Fonseca, R Ovalle, M D Lima, M H Hague, Y N Garstein, M Zhang, A A Zakhidov, R H Baughman *Science* **323** 1575 (2009)
165. A A Zakhidov, D-S Suh, A A Kuznetsov, J N Barisci, E Muñoz, A B Dalton, S Collins, H Von Ebron, M Zhang, J P Ferraris, A A Zakhidov, R H Baughman *Adv. Funct. Mater.* **19** 2266 (2009)
166. J Im, I H Lee, B Kim, J Park, W Yu, U J Kim, Y H Lee, M J Seong, E H Lee, Y S Yin, S Hong *Appl. Phys. Lett.* **94** 053109 (2009)
167. A Izadi-Najafabadi, S Yasuda, K Kobashi, T Yamada, D N Futaba, H Hatori, M Yumura, S Iijima, K Hata *Adv. Mater.* **22** E235 (2010)
168. K I Winey, R A Vaia *MRS Bull.* **32** 314 (2007)
169. E G Rakov *Vse Materialy. Entsiklop. Sprav.* (1) 11 (2010)
170. E Pfautsch *Challenges in Commercializing Carbon Nanotube Composites* (Los Angeles, New York, Cleveland, Copenhagen: World Institute of Scientology Enterprises, 2007)
171. *Nanocomposites to 2011: Demand and Sales Forecasts, Markets Share, Market Size, Market Leaders* (Cleveland: Freedonia Group, 2011)
172. *World Nanocomposites Market. Nanocomposites MCP-1526, London, 2008*
173. J-H Du, J Bai, H-M Cheng *Exp. Polym. Lett.* **1** (5) 253 (2007)
174. M C Weisenberger, R Andrews, T Rantell, in *Physical Properties of Polymers Handbook* (Ed. J E Mark) (New York: Springer, 2007) p. 585
175. K Mylvaganam, L C Zhang *Recent Patents Nanotechnol.* **1** 59 (2007)
176. S V Ahir, Y Y Huang, E M Terentjev *Polymer* **49** 3841 (2008)
177. W Wang, P Ciselli, E Kuznetsov, T Peijis, A H Barber *Philos. Trans. R. Soc. London, Ser. A* **366** 1613 (2008)
178. W Bauhofer, J Z Kovacs *Compos. Sci. Technol.* **69** 1486 (2009)
179. A L Martínez-Hernández, C Velasco-Santos, V M Castaño *Curr. Nanosci.* **6** 12 (2010)
180. N G Sahoo, S Rana, J W Cho, L Li, S H Chan *Prog. Polym. Sci.* **35** 837 (2010)
181. Z Spitalsky, D Tasis, K Papagelis, C Galiotis *Prog. Polym. Sci.* **35** 357 (2010)
182. C McClory, S J Chin, T McNally *Aust. J. Chem.* **62** 762 (2009)
183. E R Badamshina, M P Gafurova, Ya I Estrin *Russ. Chem. Rev.* **79** 945 (2010)
184. V I Irzhak *Russ. Chem. Rev.* **80** 921 (2011)
185. S E O'Donnell, in *AUAA's 3rd Annual Aviation Technology, Integration and Operation (ATIO) Forum* (Denver, CO: Amer. Inst. Aeronaut. Astronaut, 2003) Techical Papers
186. S E O'Donnell, D B Smith, in *Potential Impact of Carbon Nanotube Reinforced Polymer Composite on Commercial Heavy Aircraft (Report)* (McLean, VA: MITRE Corp., 2005) p. 35
187. M D Taczak, in *A Brief Review of Nanomaterials for Aerospace Application: Carbon Nanotube-Reinforced Polymer Composites* (McLean, VA: MITRE Corp., 2006) p. 9
188. J H Koo *Polymer Nanokomposites. Processing, Characterization, and Applications* (New York, Chicago, San Francisco: McGraw-Hill, 2006)
189. M Kireitseu, D Hui, G R Tomlinson *Composites, B* **39** 128 (2008)

190. L Ci, J Suhr, V Pushparaj, X Zhang, P M Ajayan *Nano Lett.* **8** 2762 (2008)
191. J Suhr, N A Koratkar *J. Mater. Sci.* **43** 4370 (2008)
192. B Bhushan *J. Phys.: Condens. Matter* **20** 365214 (2008)
193. V A Kovtun, V N Pasovets *Trenie i iznos* **27** 206 (2006)
194. J K W Sandler, J E Kirk, I A Kinloch, M S P Shaffer, A H Windle *Polymer* **44** 5893 (2003)
195. J G Smith Jr, J W Cornell, D M Delozier, K A Watson, E Bekyarova, A Yu, R C Haddon *High Perform. Polym.* **20** 567 (2008)
196. T-W Chou, E T Thostensen *Adv. Mater.* **18** 2837 (2006)
197. D Cai, M Song *Carbon* **44** 2107 (2008)
198. B H Cipiriano, T Kashiwagi, S R Raghavan, Y Yang, E A Grulke, K Yamamoto, J R Shields, J F Douglas *Polymer* **48** 6086 (2007)
199. T Kashiwagi, F Du, K I Winey, K M Groth, J R Shields, S P Bellayer, H Kim, J F Douglas *Polymer* **46** 471 (2005)
200. T Kashiwagi, F Du, J F Douglas, K I Winey, R H Harris, J R Shields *Nature Mater.* **4** 928 (2005)
201. S Bocchini, A Frache, G Camino, M Claes *Eur. Polym. J.* **43** 3222 (2007)
202. T Kashiwagi, E Grulke, J Hilding, K Groth, R Harris, K Butler, J Shields, S Kharchenko, J Douglas *Polymer* **45** 4227 (2004)
203. B Schartel, P Potschke, U Knoll, M Abdel-Goad *Eur. Polym. J.* **41** 1061 (2005)
204. S Peeterbroeck, F Laoutid, J M Taulemesse, T Monteverde, J M Lopez-Cuesta, J B Nagy, M Alexandre, P Dubois *Adv. Funct. Mater.* **17** 2787 (2007)
205. S-H Liao, C-C Weng, C-Y Yen, M-C Hsiao, C-C M Ma, M-C Tsai, A Su, M-Y Yen, Y-F Lin, P L Liu *J. Power Sources* **195** 263 (2010)
206. L Dai *Aust. J. Chem.* **60** 472 (2006)
207. U Yogeswaran, S M Chen *Anal. Lett.* **41** 210 (2008)
208. Rajesh, T Ahuya, D Kumar *Sens. Actuators, B* **136** 275 (2009)
209. R H Baughman, C Cui, A A Zakhidov, Z Iqbal, J N Bariski, G M Spinks, G G Wallace, A Mazzoldi, D De Rossi, A G Rinzler, O Jaschinski, S Roth, M Kertesz *Science* **284** 1340 (1999)
210. H Koerner, G Price, N A Pearce, M Alexander, R A Vaia *Nature Mater.* **3** 115 (2004)
211. L Chen, C Liu, K Liu, C Meng, C Hu, J Wang, S Fan *ACS Nano* **5** 1588 (2011)
212. Y Chen, Y Lin, Y Liu, J Doyle, N He, X Zhuang, J Bai, W J Blau *J. Nanosci. Nanotechnol.* **7** 1268 (2007)
213. M A Solodyankin, E D Obraztsova, A S Lobach, A I Chernov, A V Tausenev, V I Konov, E M Dianov *Opt. Lett.* **33** 1336 (2008)
214. M Cho, J Jang, J Suhr *J. Nanosci. Nanotechnol.* **11** 1098 (2011)
215. T Hasan, Z Sun, F Wang, F Bonaccorso, P H Tan, A G Rozhin, A C Ferrari *Adv. Mater.* **21** 3874 (2009)
216. B Ashrafi, J Guan, V Mirjali, P Hubert, B Simard, A Johnston *Composites, A* **41** 1184 (2010)
217. C-H Tsai, C Zhang, D A Jack, B Wang, R Liang *J. Nanosci. Nanotechnol.* **11** 2132 (2011)
218. Y J Jung, S Kar, S Talapatra, C Soldano, G Viswanathan, X Li, Z Yao, F S Ou, A Avadhanula, R Vajtai, S Curran, O Nalamasu, P M Ajayan *Nano Lett.* **6** 413 (2006)
219. B L Wardle, D S Saito, E J García, A J Hart, R G de Villoria, E A Verploegen *Adv. Mater.* **20** 2707 (2008)
220. N Thongprachan, K Nakagawa, N Sano, T Charinpanitkul, W Tanthapanichakoon *Mater. Chem. Phys.* **112** 262 (2008)
221. R C Tenent, T M Barnes, J D Bergeson, A J Ferguson, B To, L M Gedvilas, M J Heben, J L Blackburn *Adv. Mater.* **21** 3210 (2009)
222. M K Shin, J Oh, M Lima, M E Kozlov, S J Kim, R N Baughman *Adv. Mater.* **22** 2663 (2010)
223. C Luo, X Zuo, L Wang, E Wang, S Song, J Wang, J Wang, C Fan, Y Cao *Nano Lett.* **8** 4454 (2008)
224. M Imai, K Akiyama, T Tanaka, E Sano *Compos. Sci. Technol.* **70** 1564 (2010)
225. S H Tan, Y Cho, W Lee, N Lee, S C Hong *J. Nanosci. Nanotechnol.* **11** 3350 (2011)
226. X Yu, R Rajamani, K A Stelson, T Cui *Sens. Actuators* **132** 626 (2006)
227. B J Hinds, N Chopra, T Rantell, R Andrews, V Gavalas, L G Bachas *Science* **303** 62 (2004)
228. A F Ismail, P S Goh, S M Sanir, M Aziz *Sep. Purific. Technol.* **70** 12 (2009)
229. M S Mauter, M Elimelech, C O Osuji *ACS Nano* **4** 6651 (2010)
230. M Naraghi, T Filleter, A Noravsky, M Locascio, R Oloutfi, H D Espinosa *ACS Nano* **4** 6463 (2010)
231. W Ma, L Liu, Z Zhang, R Yang, G Liu, T Zhang, X An, X Yi, Y Ren, Z Niu, J Li, H Dong, W Zhou, P M Ajayan, S Xie *Nano Lett.* **9** 2855 (2009)
232. D Blond, W Walshe, K Young, F M Blinge, U Khan, D Almecija, L Carpenter, J McCauley, W J Blau, J N Coleman *Adv. Funct. Mater.* **18** 2618 (2008)
233. S S Samal, S Bal *J. Miner. Mater. Charact. Eng.* **7** 355 (2008)
234. A R Boccaccini, J Cho, T Subhani, C Kaya, F Kaya *J. Eur. Ceram. Soc.* **30** 115 (2010)
235. J Cho, A R Boccaccini, M S P Shaffer *J. Mater. Sci.* **44** 1934 (2009)
236. P Hvizdoš, V Puchý, A Duszová, J Dusza, in *Nanofibers — Production, Properties and Functional Applications* (Onine Ed.) (Ed. T Lin) (Vienna: InTech., 2011) p. 241
237. U S Shin, I-K Yoon, G-S Lee, W-C Jang, J C Knowles, H-W Kim *J. Tissue Eng.* **2011** 674287 (2011)
238. S J Gill, A M Shobe, L J Hoppe-Weeks *Scanning* **31** 132 (2009)
239. N P Padture *Adv. Mater.* **21** 1 (2009)
240. A Datye, K-H Wu, G Gomes, V Monroy, H-T Lin, J Vleugels, K Vanmeensel *Compos. Sci. Technol.* **70** 2086 (2010)
241. G Yamamoto, M Omori, K Yokomizo, T Hashida *Diamond Relat. Mater.* **17** 1554 (2008)
242. Y Chen, A Samant, K Balani, N B Dahorte, A Agarwal *Appl. Phys., A* **94** 861 (2009)
243. H-Z Wang, X-D Li, J Ma, G-Y Li, T-J Hu *Composites, A* **43** 317 (2012)
244. J M Makar, J J Beaudoin, in *The 1st International Symposium on Nanotechnology in Construction, Pausley, Scotland, 2003* p. 331
245. L Raki, J J Beaudoin, R Alizadeh, J Makar, T Sato *Materials* **3** 918 (2010)
246. B Han, X Yu, J Ou, in *Nanotechnology in Civil Infrastructure. A Paradigm Shift* (Eds K Gopalakrishnan, B Birgisson, P Taylor, N O Attoh-Okine) (New York: Springer, 2011) p. 1
247. S J Chen, F G Collins, A J N Macleod, Z Pan, W H Duan, C M Wang *IES J., A* **4** (4) 254 (2011)
248. K Wille, K J Loh *J. Transp. Res. Rec.* **2142** 119 (2010)
249. G Y Li, P M Wang, X Zhao *Carbon* **43** 1239 (2005)
250. A Cwirzen, K H Cwirzen, V Penttala *Adv. Cem. Res.* **20** 65 (2008)
251. P R Mudimela, L I Nasibulina, A G Nasibulin, A Cwirzen, M Valkeapää, K Habermehl-Cwirzen, J E M Malm, M J Karppinen, V Penttala, T S Koltsova, O V Tolochko, E I Kauppinen *J. Nanomater.* 526128 (2009)
252. S Musso, J M Tulliani, G Ferro, A Tagliaferro *Compos. Sci. Technol.* **69** 1985 (2009)
253. A Chaipanich, T Nochaiya, W Wongkeo, P Torkittikul *Mater. Sci. Eng., A* **527** 1063 (2010)
254. M S Konsta-Gdoutos, Z S Metaxa, S P Shah *Cem. Concr. Compos.* **32** 110 (2010)
255. T Nochaiya, P Torkidtikul, P Singjai, A Chaipanich *Adv. Mater. Res.* **55** 549 (2008)

256. T Nochaiya, A Chaipanich *Appl. Surf. Sci.* **257** 1941 (2010)
257. G I Yakovlev, G N Pervushin, A Korzhenko, A F Bur'yanov, I A Pudov, A A Lushnikova *Stroit. Mater.* **2** 47 (2011)
258. L I Nasibulina, P R Mudimela, A G Nasibulin, T S Kol'tsova, O V Tolochko, E I Kauppinen *Vopr. Materialoved.* **1** 121 (2010)
259. V V Golubkov, E N Potapova, E G Rakov, in *Nauchnaya Sessiya NIYaUI MIFI-2012. Annotatsii Dokladov* (Research Session of NIYaUI MIFI-2012. Abstracts of Reports) (Moscow: National Research Nuclear University Moscow Engineering Physics Institute, 2012) Vol. 1, p. 186
260. Z S Metaxa, J-W T Seo, M S Konsta-Gdoutos, M C Hersam, S P Shah *Cem. Concr. Compos.* **34** 612 (2012)
261. B M Tyson, R K Abu Al-Rub, A Yardanbakhsh, Z Grasley *J. Mater. Civil Eng.* **23** 1028 (2011)
262. C Gay, F Sanchez *J. Transp. Res. Board.* **2142** 109 (2010)
263. J M Makar, G W Chan *J. Am. Ceram. Soc.* **92** 1303 (2009)
264. X Yao, C Wu, A Du, J Zou, Z Zhu, P Wang, H Cheng, S Smith, G Lu *J. Am. Chem. Soc.* **129** 15650 (2007)
265. A Agarwal, S R Bakshi, D Lahiri *Carbon Nanotubes: Reinforced Metal Matrix Composites* (Boka Raton, FL: CRC Press, 2010)
266. S R Bakshi, D Lahiri, A Agarwal *Int. Mater. Rev.* **55** 41 (2010)
267. H Dieringa *J. Mater. Sci.* **46** 289 (2011)
268. W M Daoush *Powder Metall. Met. Ceram.* **47** 531 (2008)
269. W M Daoush, B K Lim, C B Mo, D H Ham, S H Hong *Mater. Sci. Eng. A* **513–514** 247 (2009)
270. K Chu, Q Wu, C Jia, X Liang, J Nie, W Tian, G Gai, H Guo *Compos. Sci. Technol.* **70** 298 (2010)
271. P Quang, Y G Jeong, S C Yoon, S I Hong, S H Hong, H S Kim *Mater. Sci. Forum* **534–536** 245 (2007)
272. W X Chen, J P Tu, L Y Wang, H Y Gan, Z D Xu, X B Zhang *Carbon* **41** 215 (2003)
273. S M Uddin, T Mahmud, C Wolf, C Glanz, I Kolaric, M Hulman, E Neubauer, S Roth *Phys. Status Solidi, B* **246** 2836 (2009)
274. T Laha, Y Liu, A Agarwal *J. Nanosci. Nanotechnol.* **7** 515 (2007)
275. T Laha, A Agarwal *Mater. Sci. Eng., A* **480** 323 (2008)
276. S Arai, M Endo, T Sato, A Koide *Electrodepos. Solid-State Lett.* **9** C131 (2006)
277. S Salimi, H Izadi, A P Gerlich *J. Mater. Sci.* **46** 409 (2010)
278. A Izadi-Najafabadi, T Yamada, D N Futaba, M Yudasaka, H Takagi, H Hatori, S Iijima, K Hata *ACS Nano* **5** 811 (2011)
279. P J King, U Khan, M Lotya, S De, J N Coleman *ACS Nano* **4** 4238 (2010)
280. T-K Hong, D W Lee, H J Choi, H S Shih, B-S Kim *ACS Nano* **4** 3861 (2010)
281. D H Lee, J E Kim, T H Han, J W Hwang, S Jeon, S-Y Choi, S H Hong, W J Lee, R S,Ruoff, S O Kim *Adv. Mater.* **22** 1247 (2010)
282. Z Fan, J Yan, L Zhi, Q Zhang, T Wei, J Feng, M Zhang, W Qian, F Wei *Adv. Mater.* **22** 3723 (2010)
283. Z-J Fan, J Yan, T Wei, G-Q Ning, L-J Zhi, J-C Liu, D-X Cao, G-L Wang, F Wei *ACS Nano* **5** 2787 (2011)
284. J Zhao, Q Guo, J Shi, L Liu, J Jia, Y Liu, H Wang *Carbon* **47** 1747 (2009)
285. C-C Chuang, W-L Liu, W-J Chen, J-H Huang *Int. J. Miner. Metall. Mater.* **16** 128 (2009)
286. H Y Jung, S M Jung, J S Suh *Carbon* **46** 1345 (2008)
287. B Wu, Q-M Gong, J-J Wu, H-H Song, J Liang *Trans. Nonferrous Met. Soc. China* **19** 646 (2009)
288. C M Leroy, F Carn, R Backov, M Trinquecoste, P Delhaes *Carbon* **45** 2317 (2007)
289. T Bordjiba, M Mohamedi, L H Dao *J. Power Sources* **172** 991 (2007)
290. M A Worsley, J H Satcher Jr, T F Baumann *Langmuir* **24** 9763 (2008)
291. T Bordjiba, M Mohamedi, L H Dao *J. Electrochem. Soc., A* **155** 115 (2008)
292. M A Worsley, P J Pauzauskie, S O Kucheyev, J M Zaug, A V Hamza, J H Satcher Jr, T F Baumann *Acta Mater.* **57** 5131 (2009)
293. M A Worsley, S O Kucheyev, J H Satcher, A V Hamza, T F Baumann *Appl. Phys. Lett.* **94** 073115 (2009)
294. T Bordjiba, M Mohamedi *J. Solid State Electrochem.* **15** 765 (2010)
295. D-J Kim, J-W Park, J-S Kim, K-K Cho, K-W Kim, J-H Ahn, M-K Jo, H-J Choi, D-H Bae, H-J Ahn *J. Nanosci. Nanotechnol.* **11** 484 (2011)
296. T V Sreekumar, T Liu, B G Min, H Guo, S Kumar, R H Hauge, R E Smalley *Adv. Mater.* **16** 58 (2004)
297. M Lisunova, A Hildmann, B Hatting, V Datsyuk, S Reich *Compos. Sci. Technol.* **70** 1584 (2010)
298. Z-G Zhao, L-J Ci, H-M Cheng, J-B Bai *Carbon* **43** 663 (2005)
299. M Al-Haik, C C Luhrs, M M R Taha, A K Roy, L Dai, J Phillips, S Doom *J. Nanotechnol.* **2010** 860178 (2010)
300. A Godara, L Gorbatikh, G Kalinka, A Warrier, O Rochez, L Mezzo, F Luizi, A W van Vuure, S V Lomov, I Verpoest *Compos. Sci. Technol.* **70** 1346 (2010)
301. S S Wicks, R Guzman de Villoria, B L Wardle *Compos. Sci. Technol.* **70** 20 (2010)
302. Q-J Gong, H-J Li, X Wang, Q-G Fu, Z-W Wang, K-Z Li *Compos. Sci. Technol.* **67** 2986 (2007)
303. J L Abot, Y Song, M J Schulz, V N Shanov *Compos. Sci. Technol.* **68** 2755 (2008)
304. T Yokozeki, Y Iwahori, S Ishiwata, K Enomoto *Composites, A* **38** 2121 (2007)
305. L Sun, Y Zhao, Y Duan, Z Zhang *Chin. J. Aeronaut.* **21** 361 (2008)
306. W-J Chen, Y-L Li, C-L Chiang, C-F Kuan, H-C Kuan, T-T Lin, M-C Yip *J. Phys. Chem. Solids* **71** 431 (2010)
307. D C Davis, J W Wilkerson, J Zhu, D O O Ayewan *Compos. Struct.* **92** 2653 (2010)
308. Y Wang, Z Xu, L Chen, Y Jiao, X Wu *Polym. Compos.* **32** 159 (2011)
309. Q Cheng, B Wang, C Zhang, Z Liang *Small* **6** 763 (2010)
310. A Misra, J R Raney, L De Nardo, A E Craig, C Daraio *ACS Nano* **5** 7713 (2011)
311. P Podsiadlo, B S Shim, N A Kotov *Coord. Chem. Rev.* **253** 2935 (2009)
312. Y Rachmadini, V B C Tan, T E Tay *J. Reinf. Plast. Compos.* **29** 2782 (2010)
313. E J Garcia, B L Wardle, A J Hart *Composites, A* **39** 1065 (2008)
314. H Qian, E S Greenhalgh, M S P Shaffer, A Bismarck *J. Mater. Chem.* **20** 4751 (2010)
315. L Gao, E T Thostenson, Z Zhang, J-H Byun, T-W Chou *Philos. Mag.* **90** (31–32 Spec. Iss.) 4085 (2010)
316. L Blger, M H G Wichmann, L O Meyer, K Schulte *Compos. Sci. Technol.* **68** 1886 (2008)
317. K J Loh, J Kim, J P Lynch, N W S Kam, N A Kotov *Smart Mater. Struct.* **16** 429 (2007)
318. A Yu, P Ramesh, X Sun, E Brkyarova, M E Itkis, R C Haddon *Adv. Mater.* **20** 4740 (2008)
319. H Chang, M-J Kao, K-D Huang, C-G Kuo, S-Y Huang *J. Nanosci. Nanotechnol.* **11** 1754 (2011)
320. E D Laird, W Wang, S Cheng, B Li, V Presser, B Dyatkin, Yu Gogotsi, C Y Li *ACS Nano* **6** 1204 (2012)
321. M De, P S Ghosh, V M Rotello *Adv. Mater.* **20** 4225 (2008)
322. M Foldvari *Key Eng. Mater.* **441** 53 (2010)
323. Y Lee, K E Geckeler *Adv. Mater.* **22** 4076 (2010)
324. J Wang *Electroanalysis* **17** 7 (2005)
325. Q Tan, K Zhang, S Gu, J Ren *Appl. Surf. Sci.* **255** 7036 (2009)

326. T Leng, P Huie, K V Bilbao, M S Blumenkranz, D J Loftus, H A Fishman *Invest. Ophtalmol. Vis. Sci.* **44** (E-abstr.) 481 (2003)
327. M P Mattson, R C Haddon, A M Rao *J. Mol. Neurosci.* **14** 175 (2000)
328. H Hu, Y Ni, V Montana, R C Haddon, V Parpura *Nano Lett.* **4** 507 (2004)
329. T J Webster, M C Waid, J L McKenzie, R L Price, J U Ejiofor *Nanotechnology* **15** 48 (2004)
330. H Hu, Y Ni, S K Mandal, V Montana, B Zhao, R C Haddon, V Parpura *J. Phys. Chem., B* **109** 4285 (2005)
331. L P Zanello, B Zhao, H Hu, R C Haddon *Nano Lett.* **6** 562 (2006)
332. S L Edwards, J S Church, J A Werkmeister, J A M Ramshaw *Biomaterials* **30** 1725 (2009)
333. E B Malarkey, K A Fisher, E Bekyarova, W Liu, R C Haddon, V Parpura *Nano Lett.* **9** 264 (2009)
334. A Boccaccini *Key Eng. Mater.* **441** 31 (2010)
335. R A MacDonald, B F Laurenzi, G Viswanathan, P M Ajayan, J P Stegermann *J. Biomed. Mater. Res., A* **74** 489 (2005)
336. E E Da Silva, H H M Della Colletta, A S Ferlauto, R L Moreira, R R Resende, S Oliveira, G T Kitten, R G Lacerda, L O Ladeira *Nano Res.* **2** 462 (2009)
337. A Abarrategi, M Gutiérrez, C Moreno-Vicente, M J Hortigüela, V Ramos, J L López-Lacomba, M L Ferrer, F del Monte *Biomaterials* **29** 94 (2008)
338. F L Jia, J M Gong, K W Wong, R X Du *Nanotechnology* **20** 015701 (2009)
339. Z Moridi, V Mottaghitalab, A K Haghi *Cellulose Chem. Technol.* **45** 549 (2011)
340. T J Simmons, S-H Lee, T-J Park, D P Hashim, P M Ajayan, R J Linhardt *Carbon* **47** 1561 (2009)
341. L Wu, J Lei, X Zhang, H Ju *Biosens. Bioelectron.* **24** 644 (2008)
342. J Wang *Electroanalysis* **17** 7 (2005)
343. Y Wang, Z Iqbal *JOM J. Miner. Met. Mater. Soc.* **57** (6) 27 (2006)
344. I Capek *Adv. Coll. Interf. Sci.* **150** 63 (2009)
345. Y Hu, W Chen, L Lu, C Chang *ACS Nano* **4** 3498 (2010)
346. M Vila, M Manzano, M Vallet-Regi *Key Eng. Mater.* **441** 3 (2010)
347. D Tasis, N Tagmatarchis, V Georgakilas, M Prato *Chem. – Eur. J.* **9** 4000 (2003)
348. N Nakashima *Int. J. Nanosci.* **4** 119 (2005)
349. N Nakashima, T Fujigaya *Chem. Lett.* **36** 692 (2007)
350. E G Rakov, in *Nanomaterial Handbook* (Ed. Yu Gogotsi) (Boka Raton, FL, London, New York: CRC Press, 2006) p. 105
351. S Schymura, M Kühnast, V Lutz, S Jagiella, U Dettlaff-Weglikowska, S Roth, F Giesselman, C Tschierke, G Scalia, J Lagerwall *Adv. Funct. Mater.* **20** 3350 (2010)
352. P-C Ma, N A Siddiqui, G Marom, J-K Kim *Composites, A* **41** 1345 (2010)
353. E Vázques, M Prato *ACS Nano* **3** 3819 (2009)
354. J Liu, A G Rinzler, H Dai, J H Hafner, R K Bradley, P J Boul, A Lu, T Iverson, K Shelimov, C B Huffman, F Rodriguez-Macias, Y-S Shon, T R Lee, D T Colbert, R E Smalley *Science* **280** 1253 (1998)
355. J Chen, M A Hamon, H Hu, Y Chen, A M Rao, P C Eklund, R C Haddon *Science* **282** 95 (1998)
356. J Chen, A M Rao, S Lyuksyutov, M E Itkis, M A Hamon, H Hu, R W Cohn, P C Eklund, D T Colbert, R E Smalley, R C Haddon *J. Phys. Chem., B* **105** 2525 (2001)
357. J Hilding, E A Grulke, Z G Zhang, F Lockwood *J. Dispers. Sci. Technol.* **24** 1 (2003)
358. V A Davis, L M Ericson, A Nicholas G Parra-Vasquez, H Fan, Y Wang, V Prieto, J A Longoria, S Ramesh, R K Saini, C Kittrell, W E Billups, W W Adams, R H Hauge, R E Smalley, M Pasquali *Macromolecules* **37** 154 (2004)
359. A N Parra-Vasquez, N Behabtu, M J Green, C L Pint, C C Young, J Schmidt, E Kesselman, A Goyal, P M Ajayan, Y Cohen, Y Talmon, R H Hauge, M Pasquali *ACS Nano* **4** 3969 (2010)
360. F Liang, A K Sadana, A Peera, J Chattopadhyay, Z Gu, R H Hauge, W E Billups *Nano Lett.* **4** 1257 (2004)
361. A B Bourlinos, V Georgakilas, V Tzitzios, N Boukos, R Herrera, E P Giannelis *Small* **2** 1188 (2006)
362. A B Bourlinos, V Georgakilas, N Boukos, P Dallas, C Trapalis, E P Giannelis *Carbon* **45** 1583 (2007)
363. R G de Villoria, S L Figueredo, A J Hart, S A Steiner III, A H Slocum, B L Wardle *Nanotechnology* **20** 405611 (2009)
364. R Xiang, G Luo, W Qian, Y Wang, F Wei, Q Li *Chem. Vap. Deposition* **13** 533 (2007)
365. Q Zhang, J Q Huang, F Wei, G H Xu, Y Wang, W-Z Qian, D Z Wang *Chin. Sci. Bull.* **52** 2896 (2007)
366. Q Zhang, J-Q Huang, M-Q Zhao, W-Z Qian, Y Wang, F Wei *Carbon* **46** 1152 (2008)
367. U K Gautam, P M F J Costa, Y Bando, X Fang, L Li, M Imura, D Golberg *Sci. Technol. Adv. Mater.* **11** 054501 (2010)
368. E G Rakov *Russ. Chem. Rev.* **70** 827 (2001)
369. D Eder *Chem. Rev.* **110** 1348 (2010)
370. A A Eliseev, M V Kharlamova, M V Chernysheva, A V Lukashchin, Yu D Tretyakov, A S Kumskov, N A Kiselev *Russ. Chem. Rev.* **78** 855 (2009)
371. X Li, Y Qin, S T Picraux, Z-X Guo *J. Mater. Chem.* **21** 7527 (2011)
372. K Pal, D J Kang, Z X Zhang, J K Kim *Langmuir* **26** 3609 (2010)

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[b] — *Mendeleev Chem. J. (Engl. Transl.)*
[c] — *Nanotechnol. Russ. (Engl. Transl.)*
[d] — *J. Eng. Phys. Termophys. (Engl. Transl.)*